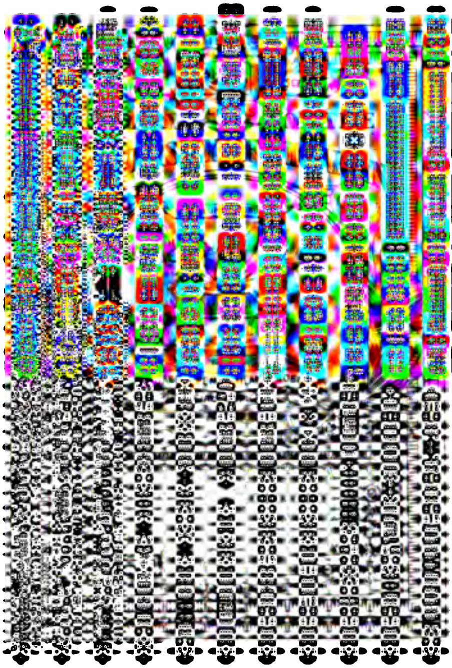

SELECT METHODS

IN

CHEMICAL ANALYSIS.

(CHIEFLY INORGANIC).

BY

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"QUARTERLY JOURNAL OF SCIENCE."

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PREFACE.

It will be perceived from the title of this work that the Author has not intended to provide the student with a complete text-book of analysis, but rather with a laboratory companion, containing information not usually found in ordinary works on Analysis. The Author has tested most of the new processes which have appeared during the last twelve years in the "Chemical News;" and as some of these have proved to be of great value, it was thought that a service would be rendered to analytical chemistry if these trustworthy methods of analysis were systematically arranged in a convenient form for laboratory use. In some instances the descriptions are given in the language of the original writer, but in all cases where the Author has improved the processes, the necessary modifications have been introduced.

It is strange that modern works on analysis should ignore about twenty of the elements. Even Fresenius gives only a separate form for their detection. Were investigators more in the habit of looking for the "rare" elements, they would no doubt turn up unexpectedly in many minerals. In the present work equal prominence is given both to the rare and to the ordinary elements.

The order in which the analytical separation of the metals is carried out will be readily understood. Take, for instance, the case of copper. After giving the best method for the detection and quantitative estimation of this metal, comes a description of the processes for separating it from those metals which have been previously passed under review, as mercury, silver, and zinc; but no attention is paid to the separation of copper from such metals as lead, tin, &c., which have not previously been treated of. Under the respective headings "Lead" and "Tin," the separation of these metals from copper is described.

A complete list of separations has not been attempted. Where no process of separation or estimation is given, it may be inferred that the Author has had no experience in any but the well-known methods employed in most laboratories; and to have introduced these ordinary processes into the work simply for the sake of filling up gaps would have largely increased its bulk without adding materially to its value. To save space, the description of a process is frequently discontinued at the point where the substances under separation are brought to such a state that the concluding steps are obvious.

No special system of weights and measures has been employed; many of the descriptions having been condensed from the original memoirs, it was thought better to retain the system therein adopted, so as to have simple numbers to deal with, instead of having to convert them to one common scale and to introduce decimals; thus—when an author says take 8 grains of a substance, 0·51816 gramme has not been substituted; and where 10 grammes are mentioned, he has not put 154·3840 grains. When not otherwise expressed, all degrees are according to the centigrade scale. Formulæ have been avoided as far as practicable.

The names of discoverers of really novel or valuable processes are mentioned; but the introduction in a laboratory guide-book of the name of every one who has contributed some trifling modification of a process would materially interfere with the concise description of the various methods, and, as a rule, such names have been omitted.

Some processes of great historic interest, as Professor Stas's method for the preparation of pure silver by distillation and otherwise, have been given in considerable detail: for this the Author thinks no apology is necessary, for it is always well for the student to have before him the highest models, in order that he may strive to attain a like perfection.

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of liquid and line of measurement), dilute these 500 grains till they measure 5000 liquid grains, and mix; 1000 measured grains of this solution contain 10 grains of the original salt.

Now, to 1000 measured grains of this solution, add excess, say 50 grains, of hydrochloric acid, if the alkalies are not present as chlorides, and pour into a shallow porcelain dish, making, with the rinsings of the measure, &c., some 1500 grains of solution. Heat the dish and contents nearly to ebullition, and add to the hot liquid so much solution of chloride of platinum as is equal to 20 grains of the metal. Evaporate this mixture on the water-bath nearly to dryness; that is, to the point when the thick syrupy liquid, on the momentary removal of the dish from the bath, passes into an orange-coloured pasty mass. At this point remove the dish from the bath, and at the same instant, and before the dish and its contents have had time to cool, drench it with 500 to 600 grains of rectified methylated spirit, containing about 15 per cent of water to 85 of the alcohols; mix rapidly by imparting a rotatory motion to the contents of the dish; then cover it and allow it to digest for five minutes. Have a filter ready, not too small, of 400 to 500 grains capacity, in a funnel with a cover; wash the filter first with hot water and then with spirit, and after a short digestion pour the alcoholic solution of the platinum salts on to the filter, draining the crystalline solid scales of the potassium salt as dry as possible, and again drench, agitate, and digest the insoluble salt with spirit; repeat this a third time, when the spirit will come away nearly colourless. Now collect the light orange crystalline scales of the chloride of platinum and potassium on the filter, by means of a wash-bottle, and, if need be, wash with spirit till it passes perfectly colourless. It is very advisable to wash the platino-potassic chloride by decantation, and finally by a stream of spirit from a wash-bottle, to avoid the use of stirrers so as to prevent the scales being broken down, and to keep both dish and funnel lightly covered till the washing is completed.

There is now nothing more to be done than to dry and weigh the platino-potassic salt, and to ignite and weigh the filter and add this to the weight of the salt. Owing, however, to the crystalline nature of the salt thus obtained, but a slight stain adheres to the filter, so that the loss by ignition is very minute and does not affect the result. As this crystalline precipitate is not hygrometric, its weight is easily and accurately determined.

In this process the following points must be chiefly attended to:—

I. Dilution of solutions.

II. Use of chloride of platinum in large excess, about 20 grains of metallic platinum to 10 grains of the salt examined.

III. Heating of solutions, and evaporation so conducted as to obtain the potassic salt in a crystalline scale-like condition.

IV. Evaporation on water-bath to a pasty condition—no further.

V. Drenching with spirit whilst the salt and dish are hot, and instantly on removal from water-bath.

VI. Washing by decantation, and avoiding breaking down of the crystalline precipitate.

In practice, the process is a rapid one, from beginning to end requiring about two hours; less time, indeed, than is frequently expended in merely washing the dense pulverulent precipitate which is obtained by the usual mode of manipulation.

The results are very accurate. The authors take 244·20 as the equivalent of the double chloride of platinum and potassium.

Precipitation of Potassium as Fluosilicate.

In some cases it is preferable to precipitate the potassium in the form of fluosilicate. This is usually effected by the addition of hydrofluosilicic acid. A great improvement on this plan has been proposed by Drs. Knop and Wolf, who employ fluosilicate of aniline as the precipitant for potassium.

To prepare this reagent, dilute the aniline with twice its volume of alcohol at 80° to 90°; then add an equal volume of saturated fluosilicated alcohol. The liquid first becomes heated, and then almost immediately solidifies. Spread the mass in a capsule, dry in the air, and reduce to powder.

This powder is composed of the desired fluosilicate, and of all the silicic acid produced during the reaction. The acid being in its insoluble modification, one washing in water suffices to separate the soluble fluosilicate of aniline from the inert silica which remains on the filter.

If coloured aniline is used, the powder must be previously washed in ether, which dissolves only the colouring matter.

Fluosilicate of aniline crystallises in nacreous scales. Soluble in water, insoluble in alcohol and ether, this salt is very useful in separating potassium from sodium, and even from ammonium, provided the liquid does not contain much excess. When this is the case the ammonia or its saline combination must first be expelled by heat.

In using this reagent, the salts are first acidulated by hydrochloric acid. Absolute alcohol is then added. On addition of an aqueous solution of fluosilicate of aniline the potassium is thus precipitated in the state of fluosilicate, even in presence of phosphoric acid.

SODIUM.

Analysis of Salt-Cake.

The method preferred for the examination of salt-cake, black-ash, soda-ash, and other commercial products of the alkali manufacture, is that given by Mr. C. R. A. Wright, B.Sc. Ordinary salt-cake is valued according to the

percentage of available sulphate of sodium contained; *i.e.*, the percentage of sulphate of sodium existing mainly as such, and partly as bisulphate of sodium. The mode of estimation of the available sulphate usually pursued is the following:—

1. The chloride of sodium is determined volumetrically by a standard silver solution.

2. The quantity of a standard alkaline solution required to render a known weight of salt-cake exactly neutral to test papers is determined, and the result sometimes calculated as anhydrous sulphuric acid, sometimes as monohydrated sulphuric acid, called "free acid."

3. The difference between the sum of the two previous determinations and 100 is assumed to be "available sulphate of sodium."

By this mode of proceeding errors of one to three or more per cent are introduced; ordinary salt-cake containing, in addition to sulphate, bisulphate and chloride of sodium, perceptible quantities of sulphate of lead, persulphate of iron, sesquioxide of iron, sulphate of calcium, sulphate of magnesium, moisture, and particles of sand, brick, &c., derived from the furnace during the manufacturing processes. Where a greater degree of accuracy is desirable, a known weight of salt-cake may be treated with water, ammonia and oxalate of ammonium added to the unfiltered solution, and the precipitated sesquioxide of iron and oxalate of calcium, with the insoluble matters, weighed after ignition: by moistening the ignited precipitate with pure sulphuric acid, and igniting again, the oxalate of calcium is converted into sulphate of calcium, and then the weight of the mixed substances indicates all the "impurities" present in the salt-cake; with the exception of the sulphate of magnesium, which rarely amounts to more than traces, and the moisture, which is occasionally a very perceptible quantity, especially in samples that have been made some length of time.

The amount of persulphate of iron present depends on the degree of heat to which the salt-cake has been subjected during manufacture. In highly roasted samples, cold water yields a solution containing no iron whatever, all the iron present in the salt-cake consequently existing as sesquioxide; specimens of under-roasted salt-cake, on the other hand, when treated with cold water, leave only fragments of brick, sulphate of lime, &c., undissolved, all the iron existing as persulphate. In ordinary salt-cake, however, there is so little ferric sulphate that no perceptible error is committed in assuming that all iron present exists as sesquioxide, and all the "free acid" as bisulphate of sodium. Accordingly, the following methods have been found to give tolerably expeditiously the exact composition of such salt-cake:—

(*a*). A known weight, 5 or 10 grammes, is dried at 110°—120° C., till constant in weight; too great elevation of temperature being avoided to prevent

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solution of a known weight, and estimating the residue left on evaporation of the filtrate and ignition with sulphuric acid; on subtraction from this of the amounts due to sulphate of magnesium, chloride of sodium, and bisulphate of sodium, the sulphate of sodium is directly ascertained.

The total "available sulphate of sodium" is known by adding $\frac{71}{120}$ of the bisulphate of sodium to the amount of sulphate of sodium found.

Black-Ash.—Commercially, the only valuable ingredient is the carbonate of sodium, the amount of which is generally determined by lixiviation of a known weight of black-ash, and titration, by normal test acid, of the liquor obtained. In manufacturing establishments it is frequently the practice to lixiviate the ash with water at some definite temperature, considered to be about the average temperature of the lixiviating vats; the liquor so obtained is examined (*a*) for alkali, determined by test acid; (*b*) for sulphate of sodium, generally estimated roughly, but with sufficient nearness for manufacturing purposes, by addition of a standard chloride of barium solution to a portion of the acidulated lixiviate, till no further precipitate is thrown down; (*c*) for sulphide, estimated by passing chlorine through the alkaline lixiviate till all sulphide is destroyed; boiling with hydrochloric acid, and volumetric determination of the sulphate as before, the increased amount representing the sulphide. Prizes are frequently given to those workmen who produce black-ash containing but little sulphate, showing a nearly complete decomposition of the salt-cake employed; and occasionally prizes are given when the sulphate after oxidation is low in amount, it being supposed that this indicates that over-roasting of the black-ash has not occurred. A slight misapprehension, however, usually attends this mode of analysis; although an over-roasted black-ash will yield a perceptible quantity of sulphide when treated with nearly absolute alcohol, yet the fact of an aqueous solution containing sulphide by no means proves that the ash was over-roasted, inasmuch as, on addition of water to black-ash, there is always a mutual reaction between the sulphide of calcium and carbonate of sodium contained therein; the amount of sulphide of sodium formed depends on the temperature and dilution of the liquid, and the time employed; and accordingly it is often found that the sulphide existing in the black-ash lye from the vats is very different in amount from that calculated from the laboratory analyses of the black-ash worked. The laboratory test for "sulphate after oxidation," therefore, is really useless, as it neither denotes the quality of work done by the furnace-man nor that of the black-ash lye.

In ordinary black-ash a sodium compound is contained* insoluble in hot water, even on long digestion, but decomposable by long-continued boiling.

* Chem. Soc. Journ., xx., 407.

In cases, therefore, where the total "available alkali" is to be exactly determined, either this long boiling must be performed, or the total sodium present must be determined gravimetrically, and that contained as chloride and sulphate subtracted; in either case a tedious operation. The same applies in the case of the analysis of the lixiviated black-ash, or vat-waste. Ordinarily, the vat-waste is examined by lixiviating or washing on a filter a known weight of waste fresh from the vats, or previously completely dried. In either case a considerable amount of sulphide of calcium comes into solution, and hence if the solution so obtained be immediately titrated with test-acid, more soda is indicated as present than really has been dissolved out. By passing carbonic acid through the solution till sulphuretted hydrogen is completely expelled, boiling to decompose bicarbonate of calcium, and filtration from the precipitated carbonate of calcium, this error is avoided. The same effect is produced by adding carbonate of ammonium to the solution, and boiling in a flask till no further evolution of ammoniacal gases takes place; but in either case the sodium contained in the insoluble compound, or as sulphate (found by oxidation of sulphide of calcium and subsequent reaction on the carbonate of sodium, especially if the waste have been previously dried), remains unestimated. When accuracy is required, therefore, a gravimetric determination of sodium is unavoidable.

In cases where an accurate analysis of the total contents of a sample of black-ash is required, the following method gives reliable results tolerably speedily. Most of the modes of determination are likewise applicable to samples of dry vat-waste:—

(*a*). A known weight is dissolved in hydrochloric acid, the insoluble coke and sand collected on a weighed filter, and the carbon subsequently burnt off.

(*b*). In the filtrate from (*a*) the sulphuric acid is estimated by precipitation by chloride of barium, and weighing the sulphate of barium.

(*c*). A known weight is dissolved in nitric acid, and the chlorine determined volumetrically by a standard silver solution.

(*d*). A known weight is treated in Mohr's carbonic acid apparatus; the carbonate of ammonium found is precipitated by boiling with chloride of calcium, the precipitate washed till the washings are neutral, dissolved in a slight excess of standard hydrochloric acid, and the excess determined by a standard alkaline solution; thus the carbonic acid can be calculated.

(*e*). A known weight is fused with four times its weight of a mixture of three parts dry carbonate of sodium and one of nitrate of potassium (both free from sulphate). From the total sulphate thus formed, and estimated gravimetrically by barium, that existing as sulphate of sodium is subtracted, and the remainder calculated as sulphur.

(*f*). A known weight is treated with hydrochloric acid, the filtrate

oxidised by nitric acid, and the mixed iron, alumina, and phosphoric acid precipitated by ammonia.

(*g*). The filtrate from (*f*) is treated with oxalate of ammonium, the precipitate estimated volumetrically by permanganate, or gravimetrically as oxalate of calcium; hence the calcium may be known.

(*h*). A known weight is lixiviated with warm water, and in the filtrate from the insoluble matter the silica is estimated by evaporation to dryness with hydrochloric acid; in the filtrate from this the aluminium combined as aluminate is determined by precipitating the alumina by ammonia.

(*i*). A known weight is cautiously treated with sulphuric acid in a capacious platinum crucible, and heated till gases cease to be evolved; the residue is treated with water, filtered, and well washed; ammonia and oxalate of ammonium are added to the filtrate; and, ultimately, the total sodium contained weighed as sulphate of sodium.

In calculating results from the foregoing data, the chlorine found is calculated as chloride of sodium, the sulphuric acid as sulphate of sodium, the silica as silicate of sodium, and the aluminium (soluble in water) as aluminate of sodium; the remaining sodium is then calculated as carbonate of sodium, and the remaining carbonic acid as carbonate of calcium. The sulphur is calculated as sulphide of calcium, and the remaining calcium as lime. From the total alumina, iron, and phosphoric acid the alumina present as aluminate is subtracted; the coke and sand, &c., are directly determined (*a*). The difference from 100 in a carefully conducted analysis will not amount to more than a few tenths per cent, and represents cyanogen, traces of moisture, &c., and loss.

In an over-roasted ash the alkaline sulphide can only be safely estimated by digestion with nearly absolute alcohol, oxidation to sulphate by chlorine, and precipitation by chloride of barium. The sodium contained as poly- or mono-sulphide, may be determined volumetrically by test acid in the alcoholic solution, and must be subtracted from that to be calculated as carbonate of sodium as above; the sulphur existing as poly- or mono- sulphide of sodium must be subtracted from the total sulphur found, the difference being calculated as sulphide of calcium.

Soda-Ash.—The commercial valuation of soda-ash is usually restricted to the determination of the percentage of "available alkali" contained therein, by this term being meant the total oxide of sodium (anhydrous) contained in a state capable of saturating a strong acid, as sulphuric; and hence including hydrate, carbonate, aluminate, silicate, sulphide, sulphite, and hyposulphite. The analysis is usually performed by adding the standard acid to the hot aqueous solution of a known weight of ash, until a slight acid reaction is obtained; by this means all the lime and the alumina contained as aluminate are estimated as though they were soda.

Practically this error is of slight importance; it may be readily avoided by addition of a very slight excess of acid along with some tincture of litmus, then adding a slight excess of standard carbonate of sodium solution, boiling and filtering from the precipitated lake and carbonate of calcium; the excess of sodium added is now again determined by the standard acid, and thus the exact amount of acid used to saturate the oxide of sodium present in the "available" state is known.

An abuse, however, that has long been practised in the soda trade in connection with this is the following:—The equivalent of sodium is considered to be 24 (instead of 23·04—Stas). Hence by varying the mode of calculation, a varying error is introduced, the available alkali being always represented as more than it really is. If sodium be thus calculated, the error is $+\frac{0\cdot96}{24}$ or 4·0 parts in 100: if oxide of sodium be calculated, the error is $\frac{64-62\cdot08}{64}$ or 3·0 parts in 100; while, if carbonate of sodium be calculated, it is $\frac{108-106\cdot08}{108}$ or 1·8 parts in 100. Hence, according to the plan employed in determining the standard of the acid used, according as sodium salts are thus used, or other substances, an error of from 0·9 to 2·0 per cent is introduced in the valuation of a 50 per cent ash.

From this arises the custom in many alkali works of invoicing the sales of ash at from 1 to 2 per cent higher than their real strength, it being known that the purchaser will accept the analytical certificate calculated on this erroneous basis. This practice is by no means universal, nor is it known to many of the purchasers of soda-ash; in certain districts, however, it prevails, and is a constant source of vexatious complaint whenever the purchaser happens to employ on his own side a more conscientious analyst. Soda-ash of identical quality has been known to be invoiced part to one customer as containing 48 per cent, part to another as 49 per cent, and part to a third as 50 per cent, the actual percentage being 48¼; the separate consignments being reported also in these different strengths by the analysts in the different towns to which the goods were sent. Inasmuch as soda-ash is usually valued as so much per cent per cwt., this amounts to a fraud on the purchaser.

Mr. Pattinson, of Newcastle-on-Tyne, has lately drawn public attention to a strange error made by some analysts in attempting to apply the English commercial test for soda to samples of alkali, soda-ash, &c., the result of which error is to make the test indicate from 1 to 1¼ per cent more soda than the sample contains by the proper English test. It is well known that the English soda-test had its origin in the early days of the soda trade—when chemists believed the equivalent of soda to be 32, and that of carbonate

of sodium 54; and consequently, test acid was made so that 40 parts of sulphuric acid neutralised 54 parts of carbonate of sodium equal to 32 of soda. This method of testing has always been, and still is, used by the soda trade throughout England; and it is a custom well understood by both buyers and sellers. It indicates 0·66 per cent more soda in a 50 per cent alkali than the rigidly-correct test based on the new equivalent 31 would indicate. It is certainly desirable, for the sake of scientific accuracy, that the correct equivalent, 31, should be used in testing; but, seeing that manufacturers have expended their capital in plant, and made their contracts for their various materials on the understanding that a product containing a certain percentage of soda would be obtained, and, seeing that there are other commercial customs of the trade still in force, which tell as much against the manufacturer as the test does in his favour—such, for instance, as that of not charging for fractions of percentages,—it is more the province of an association like the Alkali Manufacturers' Association than that of an analytical chemist to make alterations in trade usages affecting such vast interests. Certainly, if any alteration be made at all by chemists, it should be made in the direction of scientific accuracy, and not in the contrary direction, as in the case above referred to. The error arises in this way: The test-acid is made so as to indicate the exact amount of soda according to the new and correct equivalent 31—that is, that 40 parts of sulphuric acid should neutralise 53 parts of carbonate of sodium, equal to 31 parts of soda.

To convert the results obtained by this test-acid into the English commercial soda-test, it is incorrectly assumed that the 31 parts of soda are equal to 32,—in other words, that the 53 parts of carbonate of sodium contain 32 parts of soda. This is where the error lies; for, according to the correct English test, 54 parts of carbonate of sodium, and not 53, contain 32 of soda; and, therefore, by the English test, 53 parts of carbonate of sodium contain only 31·41 of soda. By thus mixing up the old and the new systems of equivalents, a sample of soda-ash which, by the correct English test, contains 50·66 per cent, would be returned as containing 51·61 per cent of soda. A sample of caustic soda which, by the correct English test would contain 75·0 per cent of soda would, by this erroneous method, indicate 76·4 per cent. It is only necessary to point out this error in order that it may be avoided and guarded against by any one interested in the buying and selling of alkalies.

When the exact composition of a sample of soda-ash is required, the following method may be adopted.

(*a*). A known weight is heated to 150°—200° C., and the loss of weight considered to be moisture.

(*b*). The residue of (*a*) treated with hydrochloric acid leaves sand and insoluble matter, and in the filtrate the sulphuric acid may be estimated volumetrically, or, better, gravimetrically by chloride of barium.

(*c*). The carbonic acid present is estimated in Mohr's apparatus, or in Fresenius and Will's, with the addition of some potassium chromate.

(*d*). A known weight is treated with water, and the solution evaporated to dryness with hydrochloric acid; thus the silica is determined: in the filtrate from this ammonia throws down alumina, from which the aluminium, as aluminate, is known.

(*e*). The insoluble residue of (*d*) with hydrochloric acid and ammonia gives the iron and alumina (not as aluminate); the filtrate from this with oxalate of ammonium gives the calcium (usually only traces).

(*f*). A known weight is dissolved in nitric acid, and the chlorine estimated by a standard silver solution.

(*g*). A known weight dissolved in water is oxidised by chlorine, and the sulphate thus formed determined; another known weight is dissolved in water and the solution divided into two equal parts; in one the iodine required to yield a blue colour when starch and acetic acid are added, is determined, to the other sulphate of zinc is added, and in the filtrate the iodine required after removal of the precipitated sulphide of zinc is again determined; from these data the sulphide, sulphite, and hyposulphite are calculable.

(*h*). The total "available alkali" is determined, the error due to the aluminium of the aluminate being eliminated as previously mentioned; subtracting from this, calculated as sodium, the sodium corresponding to the silica, alumina, sulphide, sulphite, hyphosulphite, and carbonic acid found, the difference is calculated as hydrate; this may be checked by adding chloride of barium to a known weight, and determining the amount of acid required to neutralise the filtrate: rather more hydrate is usually indicated by this mode than what is really present, owing to the presence of a portion of aluminate, hyposulphite, &c., incompletely thrown down by the barium salt.

Carefully executed analyses according to this method have yielded results adding up to between 99·8 and 100·1.

When ferrocyanide is present, it may be estimated by dissolving a known weight of ash in hydrochloric acid, and adding perchloride of iron; after standing some time, the precipitated Prussian blue may be well washed, treated with pure potash, and the ferrocyanide determined in the solution by permanganate.

M. Jean has proposed a somewhat different method of analysing soda-ash and caustic soda. His process, which, although it does not give quite so accurate results as those already described, may occasionally be found useful, is as follows:—Take 4 grms. of the sample to be analysed, and dry completely at from 110° to 120° C.; the difference between the weight of the quantity originally taken and the weight after drying gives the quantity of water.

Take 1 grm. of this dried material, place it in a glass tube, and pass a current of dry carbonic acid gas over the substance for about an hour; dry it again at 110°, to drive off any mechanically-adhering carbonic acid; place the substance upon a filter, and exhaust with tepid water, until the wash water is no longer precipitated by chloride of barium.

The filtrate is collected in a glass flask with flat bottom, and chloride of barium is added to it. The liquid is left to settle, and, on having become quite clear, is drawn off from the precipitate, by means of a pipette, and the precipitate of carbonate of barium is collected on a tared filter, washed with boiling water, dried, and weighed. If there happen to be sulphates present, the sulphuric acid is precipitated, along with the carbonate of barium, as sulphate of barium, and the weighed carbonate of barium is, therefore, washed with water acidulated with hydrochloric acid, again washed with warm water, and, after drying, weighed.

In order to estimate the carbonate of sodium, 1 grm. of the dried sample is taken, dissolved in water, precipitated with chloride of barium, the precipitate is collected on a tared filter, and after having been washed and dried, there is deducted, from the weight found, the weight of the sulphate of barium. The difference of the weights of the carbonates of barium found by these two operations indicates the quantity of carbonate of barium which, by calculation, has to be converted into caustic soda; the second assay gives the quantity of carbonate of sodium. In order to estimate the sulphide of sodium contained, 1 grm. of the dried material is again taken; this quantity is dissolved in water, and estimated according to the following process.

Estimation of Soluble Sulphides in Commercial Soda and Soda-Ash.—These may be readily estimated by the following method, based on the insolubility of sulphide of silver, and the solubility of all the other argentiferous salts, in presence of ammonia. The process was originally devised by H. Lestelle.

Prepare a normal solution of ammoniacal nitrate of silver, by dissolving 27·69 grammes of fine silver in pure nitric acid, adding 250 c.c. of ammonia, and diluting with water to bring the volume to 1 litre. Each c.c. of this solution corresponds to 0·01 gramme of monosulphide of sodium.

Dissolve the substance to be analysed in water, add ammonia, boil, and then add, drop by drop, by means of a burette divided into tenths of a c.c. the ammoniacal silver solution, and a black precipitate of sulphide of silver takes place. When nearly all the sulphur is precipitated, filter, and into the filtered liquid pour a fresh quantity of silver solution, until, after repeated filtrations, a drop of this liquid produces only a slight opacity. The estimation is then at an end, and it is only necessary to read the divisions indicated by the burette, and to convert this number into the corresponding amount of sulphide of sodium.

To estimate very small quantities of sulphide, the argentiferous liquid must be more diluted, so that each c.c. corresponds to 0·005 gramme of sulphide. The presence of chloride, sulphate, and carbonate of sodium, caustic soda, &c., makes no difference in the accuracy of this method, by reason of the solubility in ammonia of the precipitates given by these bodies with nitrate of silver.

Separation of Potassium from Sodium.

To separate potassium from sodium when in presence of sulphuric acid, Finkener proposes the following:—Add hydrochloric acid to the aqueous solution to be analysed; then solution of chloride of platinum until the liquid is deep yellow. Add water sufficient, when boiling, to dissolve the double salt precipitated; evaporate to syrupy consistence, but not dry; extract, and wash on a filter with a mixture of alcohol (specific gravity 0·8) 2 volumes, ether 1 volume. Wash well with solution of chloride of ammonium; this decomposes the sulphate of sodium and allows it to be washed away. The filtrate, alcoholic extract, and washings contain the sodium. Heat the filter and its contents in a stream of hydrogen—a temperature of 240° suffices; extract the chloride of potassium with water, and weigh or titrate with silver solution.

A great excess of sulphuric acid is to be avoided. The chloride of ammonium solution dissolves about 0·13 to 0·26 per cent of the chloride of platinum and potassium, but the quantity so lost varies with the strength of the solution, its temperature, and the quantity of free hydrochloric acid in it. On the other hand, the double salt carries down with it about 0·16—0·35 per cent of sodium salt.

Under ordinary circumstances these metals may best be separated by the method given in pp. 1, 2.

Indirect Determination of Potassium and Sodium.

The direct methods of estimating potassium and sodium—viz., by the precipitation of the former as double chloride of platinum and potassium, and reckoning sodium from the loss—though sufficiently accurate in patient and skilful hands, is yet open to many sources of error, and at the best is excedingly tedious and troublesome.

The indirect method does not appear to possess the confidence of chemists—at least, it is rarely mentioned in published investigations. Mr. P. Collier, B.A., Assistant in the Sheffield Laboratory, Yale College, U.S.A., has published (Am. Journ. Sci., xxxvii., 344) a number of experiments to ascertain the limits of error in this process.

The volumetric estimation of chlorine as perfected by Mohr offers by far the best basis for an indirect determination of the alkalies. It is, in fact,

requisite, in employing the usual direct method, to procure the alkalies in the condition of pure chlorides before precipitation.

When the alkaline chlorides are obtained free from all foreign matters, it is but the work of a few moments to ascertain their contents of chlorine.

The silver solution used for this purpose is best prepared by weighing off in a porcelain crucible about 4·8 grms. of clear crystallised nitrate of silver, fusing it at the lowest possible heat, and then ascertaining its weight accurately. After fusion it should weigh a little more than 4·7933 grms., the quantity that, contained in a litre of water, gives a solution of which 1 c.c. = 0·001 grm. of chlorine. The fused salt is dissolved in a little warm water, the solution brought into a litre flask and filled to the mark, observing the usual precautions as to temperature, &c. When thus adjusted, add to the contents of the flask, from a burette, enough water to bring the excess of nitrate of silver above 4·7933 grms. to the requisite dilution. In this way it is easy, with a burette and litre flask, to make a perfectly accurate standard solution, while this would be hardly possible should the operator weigh off less than 4·7933 grms. of nitrate of silver.

This solution, which may be preserved in a well-stoppered bottle indefinitely, without change, is next tested by means of a solution of pure chloride of sodium or chloride of ammonium; a quantity, say about 2 grains, of one of these salts being dissolved in a litre of water and 10 c.c. of the liquid taken for the comparison. The solution being ready, the estimation of chlorine is conducted as described by Mohr, Fresenius, Sutton, and others, chromate of potash being employed to indicate the completion of the reaction. The use of Erdmann's float in a burette (which may hold 70 c.c.) graduated to fifths ensures the needful accuracy of reading. Two-tenths c.c. of silver solution may be deducted as the excess needed to produce a visible quantity of chromate of silver.

From a long list of analyses given by the author, it is shown that the indirect method is in all cases equal in accuracy to the ordinary separation, while in the matter of convenience and economy of time there is no comparison between them. In no case does the difference between the quantities taken and found of either alkaline chloride exceed two milligrammes, and in most instances it is less than one milligramme. The correspondence between the amounts of chlorine as taken and found is, of course, still more near. The error that appears in the estimation of the chlorides would be considerably reduced, if, as usually happens, the metals were calculated as oxides.

The following are the formulæ employed for calculating the quantities of NaCl and KCl, or of NaO and KO, contained in or corresponding to any mixture of alkaline chlorides whose total weight and amount of chlorine are known.

W = weight of mixed chloride.
C = weight of chlorine.

$$NaCl = C \times 7{\cdot}6311 - W \times 3{\cdot}6288.$$
$$KCl = W \times 4{\cdot}6288 - C \times 7{\cdot}6311.$$
$$NaO = C \times 4{\cdot}0466 - W \times 1{\cdot}9243.$$
$$KO = W \times 2{\cdot}9243 - C \times 4{\cdot}8210.$$

LITHIUM, CÆSIUM, AND RUBIDIUM.

Lithium, Cæsium, and Rubidium, Extraction of from Lepidolite.

The following process has been found to answer well on a large scale :—Fuse the mineral at a red heat, pour it into cold water, pulverise and wash it, and treat the washed mass to twice its weight of hydrochloric acid. After several hours' boiling, separate the greater part of the silica, add nitric acid to peroxidise the iron, and precipitate by carbonate of sodium, the solution being made so weak that the carbonate of lithium will not be thrown down. After evaporation in this way in an iron vessel, to separate more carbonate of magnesium, saturate with hydrochloric acid and add the proper quantity of chloride of platinum and potassium to precipitate all the rubidium and cæsium. The filtered liquid, containing an excess of platinum and lithium, is treated with sulphuretted hydrogen to separate the platinum, then concentrated and mixed with carbonate of sodium to precipitate the carbonate of lithium. By this method 1000 parts of lepidolite will give 78 parts of carbonate of lithium, 6·5 parts of chlorides of rubidium and cæsium, supposing the operation to be continuous. The advantage of this process consists in the direct fusion of the mineral, and it may be applied to all lithian micas. If thallium is present, which is frequently the case, it will be precipitated as double chloride of platinum and thallium along with the rubidium and cæsium.

Cæsium and Rubidium, Extraction of from Mineral Waters.

Compounds of these rarer alkali metals may be separated in the following manner from saline mother liquors derived from the evaporation of some mineral waters. A boiling dilute solution of chloride of platinum added to a boiling, rather dilute solution, containing potassium, rubidium, and cæsium, will precipitate the latter metals with but a very small proportion of the first. The platinum being removed from this precipitate by means of sulphuretted hydrogen, the alkaline metals are again brought into dilute solution as chlorides; the solution is heated to boiling, and once more a dilute solution of chloride of platinum is added in two portions. After each addition the liquor is filtered, while boiling, through a water-bath filter, and the precipitate is washed with hot water; the solution is then allowed to cool

and deposit. In this way three precipitates are obtained; the first contains nearly all the cæsium, the second almost all the rubidium, and the third, deposited on cooling, is, for the most part, the potassium compound. By repeating these precipitations the compounds may be almost completely separated. The cæsium and rubidium may be finally separated from each other by one of the methods subsequently described (p. 17).

Cæsium and Rubidium, Extraction of from Lepidolite.

Dr. Oscar D. Allen, of Yale College, has shown that the lepidolite occurring at Hebron, in Maine, U.S., contains these metals in comparative abundance, and he has recommended the following process for their extraction from this mineral. The process used is based upon that employed by Professor J. Lawrence Smith, for the determination of alkalies in silicates (for this process see p. 18). Ten parts of the pulverised lepidolite are first mixed with forty parts of coarsely powdered quick-lime; a mixture of enough water to slake the quick-lime, with hydrochloric acid sufficient to form from six to seven parts of chloride of calcium is next made ready; the two mixtures are then united and stirred vigorously during the process of slaking, thus intimately blending the mineral with suitable proportions of dry hydrate of lime and chloride of calcium. Practically as good results are obtained when the lepidolite is powdered sufficiently fine to pass through a sieve of twenty holes to the linear inch, as when it is more finely pulverised; the fact being that the foliated structure of the mineral exposes a large surface to the decomposing agency of the lime mixture.

This mixture is heated to redness for six or eight hours, in Hessian crucibles. Care must be taken to avoid a heat much above redness, as otherwise alkaline chlorides volatilise in dense clouds, and the mass fusing is absorbed to a considerable extent into the crucible and lost.

The agglomerated product obtained from the ignition of this mixture is detached from the crucible, and boiled with water for a quarter to half an hour, and washed till all but a trace of the chlorides are removed. The solution thus procured, containing chloride of calcium and the chlorides of the alkali metals, is evaporated till crystals begin to form; then sulphuric acid is added as long as sulphate of calcium separates, taking care to avoid excess; and the whole mass is evaporated to dryness and strongly heated to expel free hydrochloric acid. The residue is treated with water, and the small quantity of sulphate of calcium which goes into solution precipitated with carbonate of ammonium. The filtered solution is again evaporated to dryness and ignited.

In this manner are obtained a mixture of salts, consisting of the chlorides with a small admixture of sulphates of sodium, potassium, lithium, rubidium,

and cæsium. By treating this by the process of fractional precipitation with bichloride of platinum, a mixture of the platinochlorides of cæsium and rubidium is obtained, in which no potassium can be detected with the spectroscope. The platinum salts are to be gently heated in a current of hydrogen, until a complete reduction of the platinum takes place, when the alkaline chlorides may be extracted with water.

By working in the above manner Dr. Allen obtained from 10½ kilos. of lepidolite 2169 grammes of crude alkaline chlorides, which yielded 172 grammes of mixed platinochlorides of cæsium and rubidium, equivalent to a yield of about ½ per cent of the two metals from the lepidolite.

In separating the platinum salts of cæsium and rubidium from that of potassium, a not inconsiderable amount of these metals goes into solution with the potassium salt, thus materially diminishing the quantity obtained; much the larger proportion of this loss is rubidium, due to the greater solubility of its platinum salt. This can in great measure be recovered by a repetition of the treatment.

Separation of Potassium, Sodium, and Lithium.

If potassium, sodium, and lithium are present in the same solution, first separate lithium as phosphate, and then proceed as in the separation of potassium and sodium; or convert the three into platino-chlorides, extract the sodium and lithium salts with a mixture of alcohol and ether containing a little hydrochloric acid, and wash with a mixture of absolute alcohol 6 volumes, ether 1 volume; the residue is pure chloride of platinum and potassium. Direct experiments show that the above method is not vitiated in any degree by the presence of hydrochloric, nitric, phosphoric, arsenic, or boric acids, or salts of magnesium, zinc, manganese, iron, aluminium, nickel, or copper.

Separation of Cæsium from Rubidium.

The plan recommended by Dr. Allen for separating these metals depends upon the fact that bitartrate of rubidium requires about eight times as much water for its solution as the bitartrate of cæsium, and hence they are easily separated by crystallisation.

The mixed chlorides are converted into carbonates by first converting them into sulphates, separating the sulphuric acid by caustic baryta, and removing the excess of baryta by carbonic acid. To the alkaline solution thus obtained twice as much tartaric acid is added as is necessary to neutralise it. This solution is concentrated until it is nearly saturated at 100° C. The crystals, which deposit on cooling, show the rubidium lines more intensely than did the original mixture, whilst the cæsium lines are much fainter. This product is dissolved and re-crystallised from hot saturated solutions

three times. The cæsium reaction in these successive crops diminishes until, in the fourth, it disappears, leaving the rubidium spectrum in entire purity.

The solution from which the first crystals have been removed is concentrated to nearly one-half its original volume, when, on cooling, a very small quantity of salts of the two alkalies is deposited. On repeating this operation three times, a portion of the solution, evaporated to dryness and examined by the spectroscope, gives only the lines belonging to cæsium. The several intermediate products containing both alkalies are then united, and another portion of each salt is separated from them in the same manner. By repeating this process of fractional crystallisation four times, about 90 per cent of a mixture of these alkalies may be separated in a perfectly pure state. It requires no great expenditure of time, since the solutions employed can be concentrated at high temperatures, and, on cooling, immediately deposit well formed crystals.

Bunsen's recent method for the separation of cæsium and rubidium is somewhat similar to the above, but it has the advantage that it can be effected when working on a much less bulk of material. It is as follows:—In a mixture of pure chlorides of cæsium and rubidium the chlorine is determined, and from its amount that of rubidium is calculated. The chlorides are converted into carbonates, and to the latter salts a little more tartaric acid is added than is necessary to produce neutral tartrate of cæsium and bitartrate of rubidium. The mixture, dried and pulverised, is brought upon a funnel, whose neck is stopped by a small filter, and the whole is placed in an atmosphere saturated with moisture. The neutral cæsium salt deliquesces, and passes the filter, while the acid rubidium salt remains behind.

Separation of the Alkalies from Silicates not Soluble in Acids.

One of the best processes for separating the alkalies from silicates is the one devised by Professor J. Lawrence Smith, M.D. It is sufficiently accurate to be available for their quantitative determination. This process has scarcely received the attention it deserves, and as it appears to be almost unknown in England, it is considered advisable to give the description mainly in Dr. Smith's own words rather than in a condensed abstract. After a few preliminary remarks, the Professor says that in the determination of the alkalies in silicates not soluble in acids, three important points present themselves:—

I. The means necessary to render the silicate soluble.

II. The separation of the other ingredients from the alkalies, more especially magnesia.

III. The removal of the chloride of ammonium unavoidably accumulating in the process of analysis.

I. Method of Rendering the Silicate Soluble.—To render the silicate soluble various plans have been proposed, all of which have their objections. Amongst the agents used for the purpose are baryta and several of its compounds, viz., the nitrate, carbonate, and chloride.

The first of these is undoubtedly the best decomposing agent of the four, could we use a platinum crucible to heat the mixture of it and the mineral; as it is a silver crucible is necesssary, and this is not always capable of standing the requisite heat. According to Rose, the silver crucible must be very strong, for if thin the action of a red heat might crack it, and a portion of the fused mass would ooze out through the crevices. It also may happen that a heat higher than the point of fusion of silver is necessary to a complete decomposition of the mineral. All that is here said of caustic baryta is equally applicable to nitrate of barium.

Chloride of barium has been proposed, but its decomposing properties are very feeble, as the chlorine in combination with the barium is not liberated at a white heat, and few silicates are able to produce the decomposition. It may succeed with some of the felspars, but decomposes very imperfectly even the micas. So it is rather a risk to employ it with an unknown substance.

The carbonate of barium is the compound of barium most generally employed for silica decompositions; still this is attended with much difficulty owing to the infusibility of this salt, and the impossibility of driving off the carbonic acid by heat alone; and even if this latter were possible the objection pertaining to caustic baryta would then arise.

The following extract from Rose's "Analytical Chemistry" (translation by Normandy, in a note by the translator) presents fairly the difficulties attending this method of decomposing the silicates:—

"The heat applied is so intense that some precautions must be taken. The platinum crucible containing the mixture should be exposed first to the heat of an argand lamp, and when the mass begins to agglutinate, the crucible should be closed and its cover tied down with platinum wire, then placed in a Hessian crucible, closed up also; the whole is placed upon an inverted crucible and submitted to the action of the blast of a wind furnace, beginning first gradually with a read heat, piling on more coke so as to fill up the furnace, and increasing the heat to the highest possible pitch, until the Hessian crucible begins to soften. It is absolutely necessary to the success of the operation that the Hessian crucible should be closed as well as possible, which is best done by luting the cover with fire-clay. The Hessian crucible and its cover having fused together cannot be separated except by breaking," &c., &c.

It will be seen, in reading this extract, that the heat required is not ordinarily at the command of most chemists; in fact, no other variety of

furnace than a Sefström can be depended on for a complete decomposition.

Caustic lime and its salts have also been recommended and long used for the more imperfect decomposition of silicates, as for obtaining lithia from spudomene and lepidolite. Lime or its carbonate well mixed with many silicates finely pulverised will decompose them completely at a white heat; but no one salt of calcium is capable of meeting the demand of the entire range of alkaline silicates.

In consideration of these difficulties Berzelius proposed the use of hydrofluoric acid, and this method, when applied with the numerous precautions required, will serve to decompose almost all silicates; still, according to Rose, there are siliceous compounds that cannot be completely decomposed by hydrofluoric acid. Besides, this acid is a most disagreeable one to manipulate with, whether we employ Brunner's apparatus, or Laurent's method, or what is always the best, the concentrated acid previously prepared. I may also add that the necessity of using sulphuric acid after the decomposition is made is another objectionable feature in this process.

The above furnishes a hasty review of the methods we are now possessed of for decomposing the silicates in order to determine their alkalies; their merits can be contrasted with those of the method about to be described.

The decomposing agent which I present as a substitute for all others, and as capable of meeting the demands proposed in the commencement of this description, is a mixture of carbonate of calcium and fluor spar.

Carbonate of calcium I have used for more than six years for decomposing certain of the alkaline silicates, and more successfully than carbonate of barium; still, in numerous instances, the decomposition was far from complete and the method unsatisfactory. Notwithstanding these failures, I felt convinced that lime was the most powerful decomposing agent that could be conveniently used for this purpose, as it could be used in its caustic state in a platinum crucible without injuring the latter, although exposed to the highest temperature; when its carbonate is used, a red heat sufficed to drive off the carbonic acid, and bring the mineral under the action of caustic lime, a circumstance that does not take place with carbonate of barium; and it is well that it does not, for otherwise the platinum crucible would be seriously injured.

It was evident that the only obstacle in the way of lime decomposing the silicates as thoroughly as caustic potash, was the impossibility of fusing the mixture, and thereby bringing the pulverised mineral and lime intimately in contact. This difficulty overcome, I felt confident of success. Without detailing the various methods resorted to, it will suffice to state that the object in view was to use some flux along with the mixture of the silicate and lime, which would render the mixture fluid at a bright red heat. The

two substances which recommend themselves, after many experiments, are the fluoride and chloride of calcium, neither of which have any marked decomposing action on the silicates; in fact, their action is simply that of fluxes, which enable the lime and silicate to come in contact in a liquid state, effecting nothing beyond that. It is with the fluoride of calcium that we have to do in this part of the description; for the details on the use of chloride of calcium see page 25.

The manner in which to proceed is as follows:—

Pulverise the silicate to a sufficient degree of fineness; it is not required that the levigation be carried to any great extent; mix, intimately, in a glazed porcelain mortar, a weighed portion of the mineral with 1 part of pure fluor spar and 4 to 5 parts of precipitated carbonate of calcium,* and introduce it into a platinum crucible capable of holding three times the bulk of the mixed powder. The platinum crucible should be then placed in one of earthenware, with a little magnesia on the bottom. [I always prefer the crucible made in France, called Beaufay's crucible, to enclose platinum crucibles when heated in a furnace, as their form and cleanliness make them superior to the Hessian crucible for this purpose.] The crucible may then be covered, and heated in any form of furnace where a bright red heat can be procured.

I have been using a common open portable furnace, heaping charcoal over the top of the crucible, and so easily does the effect take place that in no instance has there been a failure of complete decomposition with as simple a means of heating as the above; and I have ascertained that an alcoholic lamp with a large circular wick, urged with a bellows, will answer for making a complete decomposition of zircon in 25 minutes. This circumstance is not stated to recommend the use of a lamp for every mineral decomposition, when a simple portable furnace and charcoal are so accessible, and their effects so much more to be depended upon than a lamp. From 30 minutes to one hour's exposure to the heat is recommended.

It was an important point to test first how far this mixture could decompose the silicates, without distinction as to their containing alkalies; for it was a very simple conclusion, that if those silicates most difficult of decom-

* The fluor spar used is the transparent variety, free from all impurities; it is easily and abundantly procured in this as well as in all other countries. The carbonate of calcium is made by dissolving calc spar or pure marble in hydrochloric acid (the common acid may be used), adding an excess of the carbonate; lime-water, or milk of lime, is then poured on the solution until it is alkaline. By this means any oxide of iron, alumina, or magnesia will be thrown down. To the filtered solution, a solution of carbonate of ammonium is added, and the precipitate washed several times with distilled water. It is best to prepare one's own carbonate of calcium, for, as a general rule, little reliance can be placed on the carbonates of calcium, barium, strontium, &c., sold as being precipitated by carbonate of ammonium, for, in more than one instance, I have found the carbonate of barium sold as a carbonate of ammonium precipitate to contain sodium.

decomposition, and containing no alkalies, were completely decomposed by this process, all others must naturally give way under its action. The silicates experimented on were *zircon*, *kyanite*, *beryl*, *topaz*, *spodumene*, *margarite*, *margarodite*, and *felspars* of different descriptions. All were readily decomposed by the method just described, and without any particular care in levigating them; 1 grm. of the zircon, for instance, after being crushed in the diamond mortar, was rubbed up for 15 minutes in a large agate mortar and fused. Its complete decomposition was not only shown by its solution in hydrochloric acid, but by the amount of zirconia obtained, which was 64·8 per cent, with little iron. This concludes the first point to be considered in this description, namely, the means necessary to render the silicates soluble; the next point is the separation of the alkalies.

Separation of the other Ingredients from the Alkalies.—The platinum crucible, with its fused contents, is laid on its side in a capsule of platinum or porcelain; the latter can be used with perfect safety to the accuracy of the result. A quantity of dilute hydrochloric acid is poured into the capsule, 1 part of acid to 2 of water; the whole is heated over a lamp, when the contents of the crucible are rapidly dissolved out; the crucible is taken out and washed over the capsule; the contents of the capsule are then evaporated to dryness over a sand-bath, and, if thought necessary, it may be completed over the lamp, without danger of the spitting which occurs in the soda fusion; this evaporation to dryness is not absolutely necessary, but the advantage of it is that any great excess of hydrochloric acid is got rid of, and the precipitate in the next operation is less bulky than it otherwise would be. To the dry mass a little hydrochloric acid is added, and then 3 or 4 ozs. of water or more, as the occasion may require; it is then boiled for a short time in the same capsule, allowed to cool down a little, and then a concentrated solution of carbonate of ammonium is slowly added until there is an excess of the same; the solution becomes at first quite thick with the precipitate, but in a short time (especially with a little warming over the lamp) the precipitate accumulates in a more or less granular state, and afterwards occupies less space in the filter than the alumina it might contain (in a felspar for instance), were this latter precipitated separately by ammonia; this circumstance is of much importance in diminishing the length of the operations, and the amount of water accumulated by filtering it from several precipitates.

It will be seen that thus far the operations have been carried on in the capsule in which the fusion was dissolved. The contents of the capsule are now thrown on a filter, but before doing this it is well to pour in a little of the solution of the carbonate of ammonium, and see if the clear part of the liquid be rendered turbid; in other words, ascertain if sufficient carbonate of ammonium had been originally added.

The solution that passes through the filter contains much sal-ammoniac, the alkalies of the mineral, and a little calcium. If magnesium be one of the ingredients of the silicates examined, some of this is also present, and, in still rarer instances, some of the earths soluble in carbonate of ammonium. This last complicates in no degree the remaining steps in the analysis. It is best to let the filtrate pass into a glass flask; the washings of the filter are collected in another vessel and concentrated to a small bulk, added to the first filtrate, and the whole boiled for some time to drive off the carbonate of ammonium.* When no great haste is required in the matter, the whole filtrate (first portions as well as the washings) are collected in a beaker, and concentrated over a sand-bath. What remains now is to separate from the alkalies the substances above alluded to. I commence by getting rid of the sal-ammoniac.

The Removal of the Sal-Ammoniac unavoidably Accumulated in the Process of Analysis.—This is probably one of the greatest annoyances to the analyst in his examination of minerals: (1st) from the manner in which the salt creeps up the sides of the vessel in which the evaporation to dryness is carried on; and (2nd) from the great difficulty of preventing loss of the chlorides of the fixed alkalies mixed with sal-ammoniac. Owing to these difficulties, which my experience has often led me to contend with, the method about to be mentioned was contrived. It recommends itself both on account of its simplicity and certainty of operation.

Having some time back noticed the decomposing effect produced by heating sal-ammoniac with nitric acid, the result of the investigation was that the sal-ammoniac could be completely decomposed at a low temperature into gaseous products, and it was immediately adopted in my analytical process with the greatest satisfaction, both as to accuracy of results as well as economy of labour.

The manner of proceeding is as follows:—To the filtrate and washings concentrated in the way mentioned above, and still remaining in the flask, pure nitric acid is added, about 3 grammes of it to every gramme of sal-ammoniac supposed to exist in the liquid; a little habit will suffice to guide one in adding the nitric acid, as even a large excess has no effect on the accuracy of the analysis.

The flask is now warmed very gently, and before it reaches the boiling-point of water a gaseous decomposition will take place with great rapidity. This is caused by the decomposition of the sal-ammoniac. It is no great advantage to push the decomposition with too great rapidity; a moderately warm place on the sand-bath is best adapted for this purpose. With proper precautions the heat can be continued, and the contents of the flask

* What remains in the filter is silica, alumina, fluoride of calcium, oxide of iron, carbonate of calcium, &c.

evaporated to dryness in that vessel; but it is more judicious to pour the contents of the flask after the liquid has been reduced to ½ an oz. into a porcelain capsule (always preferring the Berlin porcelain) of about 3½ to 4 inches diameter, inverting a clean funnel of small diameter over it, and evaporating to dryness on the sand-bath or over a lamp. I prefer the latter, as at the end of the operation the heat can be increased to 400° or 500°.

By this operation, which requires no superintendence, 100 grammes of sal-ammoniac might be separated as easily and safely as 1 gramme from 5 milligrammes of alkalies, and no loss of the latter be experienced. What remains in the capsule occupies a very small bulk; this is now dissolved in the capsule with a little water (the funnel must be washed with a little water), small quantities of a solution of carbonate of ammonium added, and the solution gently evaporated nearly to dryness. This is done to separate what little lime may have escaped the first action of the carbonate of ammonium, or may have passed through the filter in solution in carbonic acid. If any of the earths soluble in carbonate of ammonium existed in the mineral, those now become separated along with the lime.

A little more water is now added to the contents of the capsule, and the whole thrown on a small filter; the filtrate as well as washings are received in a small porcelain capsule. The liquid contains only the alkalies (as chlorides and nitrates) mixed with a minute quantity of sal-ammoniac. This is evaporated to dryness over a water-bath, and then heated cautiously over the lamp, to drive off what sal-ammoniac may have formed, which is exceedingly minute if the process as pointed out be closely adhered to. It is not absolutely necessary to heat the capsule over the lamp to get rid of the sal-ammoniac, for the little sulphate of ammonium which may be formed in the step is easily removed in the final heating in a platinum vessel.

On the contents of the capsule, as taken either from the water-bath or as after being treated over the lamp, pure dilute sulphuric acid is poured (1 part acid, 2 water), and the contents boiled for a little time, when all the nitric acid and chlorine in combination with the alkalies will be expelled; the acid solution of the alkalies is now poured into a platinum capsule or crucible, evaporated to dryness, and ignited. In order to ensure complete reduction of the bisulphates into the neutral sulphates, the usual method must be adopted of throwing some pulverised carbonate of ammonium into the platinum capsule or crucible, and covering it up so as to have an ammoniacal atmosphere around the salt, which will ensure the volatilisation of the last traces of free sulphuric acid. The alkalies are now in the state of pure sulphates, and may be weighed as such.

Thus far, the mineral has been supposed to contain no magnesia. If this alkaline earth be present, take the residue as found in the capsule

dissolve it in a little water, then add sufficient pure lime-water* to render the solution alkaline; boil and filter; the magnesia will, in this simple way, be separated from the alkalies. The solution which has passed through the filter is treated with carbonate of ammonium in the manner alluded to (p. 24), and the process continued and completed as described.

The next point to be considered is the conversion of the sulphates of the alkalies into chlorides. The method ordinarily adopted to accomplish this change is to precipitate the sulphuric acid by means of chloride of barium, care being taken to avoid the slightest excess of the latter. The annoyance attendant upon this exact precipitation is familiar to all who may have had occasion to make the trial.

Instead of chloride of barium, the acetate of lead is used; a solution of this salt is poured in excess upon the solution of sulphates; warming the latter slightly, the sulphate of lead readily separates; the whole can be immediately thrown on a filter and washed; a drop or two of the acetate of lead should be added to the filtrate to ensure there being an excess of the lead salt.

The filtrate is then warmed and sulphuretted hydrogen added; care must be taken to see that there is an excess of sulphuretted hydrogen, a test most readily performed by means of a piece of lead-paper. The liquid is thrown on a filter to separate the sulphuret of lead; the filtrate containing the alkalies as acetates is evaporated, and, when nearly dry, an excess of hydrochloric acid is added, and the whole evaporated to dryness over a water-bath, and finally heated to above 250°. A hot solution of the chloride of lead can be used instead of the acetate, rendering the addition of hydrochloric acid unnecessary.

It needs but little experience to convince one of the superiority of this method over that by the chloride of barium for converting the sulphates into the chlorides, its principal recommendation being the indifference with which an excess of the lead-salt can be added to precipitate the sulphuric acid, and the subsequent facility with which that excess of lead can be got rid of. It may be well to state that experiments were made to prove the perfect precipitation of the sulphuric acid from the sulphates of the alkalies by salts of lead, and it is only after numerous comparative results that it is now recommended.

Substitution of Chloride of Ammonium for Fluoride of Calcium, to Mix with Carbonate of Lime for Decomposing the Silicates.

It was mentioned in the previous paper on this subject how carbonate of lime could be rendered as powerful in its decomposing agency on the silicates as

* If lime-water is made, it is well to make it of lime of the best quality, and the first two or three portions of distilled water shaken up should be thrown away, as containing the small amount of alkalies sometimes present in lime.

caustic potash, the effect being due to the use of some flux, fluoride and chloride of calcium being used for that purpose. I have since tested more carefully the merits of the chloride of calcium, and for various reasons prefer it to the exclusion of the fluoride. In the first place, it introduces chlorine instead of fluorine into the analysis; and secondly, the fused mass is more easily detached from the crucible, and dissolved by hydrochloric acid.

The manner of introducing the chloride of calcium into the mixture of mineral and carbonate of calcium was a point of some little importance, as from the deliquescent nature of that compound it was inconvenient to weigh and mix it with the carbonate of calcium and mineral; these difficulties are obviated by employing *chloride of ammonium* to form indirectly the chloride of calcium.

The process which appears to leave hardly anything to desire is to take *1 part of the finely pulverised mineral, 5 to 6 of carbonate of calcium, and ½ to ¾ of chloride of ammonium*;* mix them intimately in a glazed mortar, introduce the mixture in a platinum crucible, and heat to bright redness in a furnace† from 30 to 40 minutes.

There is no silicate which, after having undergone this process, is not easily dissolved by hydrochloric acid. For the action of the lime to have been complete, it is not necessary that the mass should have settled down in perfect fusion. The contents of the crucible are dissolved, and the analysis continued as pointed out in the preceding pages.

This method ensures the obtaining of every particle of the alkalies in the mineral examined, requiring no more precaution than any good analyst is expected to take in the simplest of his processes; and not the least of the advantages is the ready method of separating all the other ingredients, and the small accumulation of water arising from the little washing necessary.

A Speedy Method of Separating the Alkalies directly from the Lime-Fusion, for both Qualitative and Quantitative Determination.

As soon as the fusion with carbonate of calcium and sal-ammoniac gave evidence of the mineral being so thoroughly attacked, the question naturally arose as to the condition the alkalies were in after the fusion, and the possibility of dissolving them out by the agency of water alone, at least for the

* The chloride of ammonium is best obtained in a pulverulent condition by dissolving some of the salt in hot water, and evaporating rapidly; the greater portion of the chloride of ammonium will deposit itself in a pulverulent condition, the water is poured off, and the salt, thrown on bibulous paper, allowed to dry, the final desiccation being carried on in a water-bath, or in any other way with a corresponding temperature.

† An ordinary portable furnace with a conical sheet-iron cap of from 2 to 3 feet high answers the purpose perfectly well, all the requisite heat being afforded by it.

purpose of qualitative determination. Experiments directed to this object soon made it evident that the alkalies might be obtained from any silicate, without resorting to the use of acid as a solvent for the fusion.

The mass as it comes from the crucible is placed in a capsule with water, and then heated in a sand-bath or over a lamp for two or three hours, renewing the water from time to time as it evaporates. The mass disintegrates very shortly after being placed in the water. The contents of the capsule are next thrown on a filter, and the water passes through, containing the chloride of the alkali, a little chloride of calcium and caustic lime; all else that the mineral may have contained remains on the filter, except baryta and strontia, if they be present in the mineral; but as these oxides are of rare occurrence in silicates, no allusion will be made to them here.

To the filtrate add carbonate of ammonium, and boil for some time, when all the calcium will be precipitated as carbonate; add a few drops of a solution of carbonate of ammonium to the hot solution to be sure that all the calcium is precipitated; should this be the case, filter; the filtrate will contain the chlorides of the alkalies and chloride of ammonium; it is evaporated to dryness over a water-bath in a small platinum capsule; the capsule is carefully heated to expel the sal-ammoniac, and finally heated to about 400°; it is then weighed with its contents, and the chlorides, if mixed, separated in any convenient manner. The amount of sal-ammoniac to be expelled is quite small, not equalling the weight of mineral originally employed.

Nothing in analysis can be simpler or more speedy than this process. Its constant accuracy still lacked some little to render it perfect, as usually an amount of alkali remained behind amounting to from $\frac{8}{10}$ths to 1 per cent of the mineral used, certainly a small quantity, but still too much to be omitted in an accurate analysis. This also must be arrived at, and it can be accomplished in the following manner:—

After the fused mass has been treated with water, filtered, and washed as above, the filter and its contents are dried; the latter are detached from the filter and rubbed up in a glazed mortar with an amount of sal-ammoniac equal to one-half the weight of the mineral, and re-heated in a platinum crucible exactly as in the first instance, treated with water, thrown on a filter and washed, the filtrate added to that from the first fusion, the whole treated with carbonate of ammonium and completed as above described.

This second fusion complicates the method but little, as the residue on the filter readily dries in a water-bath into a powder that is easily detached from the filter, and the small portion adhering to the latter may be disregarded, as the alkalies remaining rarely exceed more than 1-500th

of the whole mass, and, in most instances, not more than 1-1000th. In many analyses made, one fusion sufficed for the entire extraction of the alkalies; but as a few tenths would occasionally remain behind, we preferred the additional fusion to get at that small quantity, and to entitle it to rank as a method by which all but the merest trace of the alkalies could be extracted from the insoluble silicates.

The proportion of sal-ammoniac added to the carbonate of lime as here recommended was arrived at after numerous experiments. By increasing the sal-ammoniac, and thereby augmenting the amount of chloride of calcium formed, the mass fuses more thoroughly, but the water does not disintegrate it as completely as when the ammoniacal salt is less—an object not to be disregarded.

The advantage of thus estimating the alkalies in insoluble silicates is obvious; the long routine of separating silica, alumina, lime, &c., is done away with; the accumulation of chloride of ammonium is very trifling; and lastly, the alkalies are obtained directly in the form of chlorides. The method will vie in accuracy with any other, including the one already mentioned in the first part of this description, and at the same time it is unequalled in simplicity, speed of execution, and constancy of results.

In examining for alkalies qualitatively one fusion will of course be all that is necessary, and the action of the heat need not be continued more than thirty minutes before filtering. This method will not answer when boracic acid is present in the silicate. For methods of proceeding in such a case see the chapter treating on Boron.

In a recent note on the subject of alkalies in silicates Professor Lawrence Smith gives some interesting particulars respecting the presence of rare alkalies in the mineral leucite.

The specimens of leucite examined came from four localities—Vesuvius, Andernach, Borghetta, and Frescati. They were about as good specimens as are obtained from those localities, although all of them were not equally pure. The alkalies found in each, calculated as potash, were—

Vesuvius	21·85
Andernach	20·06
Borghetta	20·68
Frescati	20·38

Although they are said to be "calculated as potash," there is a notable quantity of rubidium and cæsium present in all the specimens above mentioned. In fact, by the method adopted in testing for these alkalies, abundant indications are obtained of the presence of rubidium and cæsium (the last not so readily), even when operating on but ½ a grm. of the mineral. The quantity of these alkalies in leucite is found to be about 9-10ths of 1 per cent of the entire mineral. Of course it is not at all remarkable that

the potash in the different specimens of leucite should be the same; but it is a matter of interest to know that, from whatsoever locality it comes, this minute quantity of rubidium and cæsium occurs with it.

Determination of Alkalies in Fire-Clays and other Insoluble Silicates.

Mr. G. Gore, F.R.S., has described a modification of the hydrofluoric process of treating silicates, which had been found useful when only the alkalies are required. An intimate mixture of the finely powdered fire-clay, nitrate of baryta, and fluoride of barium is projected into a heated crucible; when all the mixture has been thrown in, the crucible is covered and gradually heated in a furnace until the contents are completely melted; the mixture is poured into a cast-iron vessel, and immediately covered over. The resulting fused mass is finely powdered, digested with sulphuric acid, evaporated to dryness, and afterwards treated in the usual manner. The results of analyses made in this manner agree with those obtained by the hydrofluoric acid process.

In the chapter on Silicates will be found other methods of analyses by which the alkalies may be separated and estimated; but the processes are mostly devised for the simultaneous estimation of many other substances, whilst at the same time they are not so simple as those here given.

AMMONIA.

Ammonia, Nessler's Test for.—This test is of great value in water analyses and other cases where the ammonia is present in minute quantities only. Mr. Hadow, Dr. W. A. Miller, Professor Frankland, and Mr. Armstrong have introduced useful modifications into the original process. The following process, which has been found to answer perfectly, is based upon the descriptions of the above chemists.

Make a concentrated solution of an ounce or more of corrosive sublimate; having dissolved 2½ ounces of potassic iodide in about 10 ounces of water, add to this the mercurial solution until the iodide of mercury ceases to be dissolved on agitation; next dissolve 6 ounces of solid hydrate of potash in its own weight of water, and add it gradually to the iodised mercurial solution, stirring whilst the mixture is being made; then dilute the liquid with distilled water till it measures one quart. When first prepared it usually s a brown colour of greater or less intensity, owing to the presence of a little ammonia; but if set aside for a day or two it becomes clear and nearly colourless; the clear liquid may then be decanted for use. For a litre of the test liquid of equal strength 62·5 grammes of potassic iodide, and 150 grammes of solid caustic potash will be required. About 50 grains (3 c.c.) of this solution are drawn off by a marked pipette and added to one-half of a solution or distillate to be tested for ammonia; if no ammonia be present

the mixture remains colourless, but if ammonia be present the liquid will assume a yellowish tinge of greater or less intensity. The liquid will remain clear if the ammonia do not exceed 1-200th of a grain in the 5 ounces, or about 0·25 mgm. in 125 grammes of the distillate. The quantity of ammonia in such a case may be very accurately estimated in the following manner:—A solution of sal-ammoniac is prepared, containing 3·17 grains of the salt in 10,000 grains of water (or 0·317 grammes of salt per litre), which is equivalent to 1-10,000th of a grain of ammonia in each grain of this solution, or 0·1 gramme in 1 litre. Suppose that a tint is obtained in the distilled liquid, which experience leads the observer to estimate, say, at 5-1000ths of a grain; 50 grains of the standard sal-ammoniac solution are placed in a beaker similar in size to that used for the distillate under trial, then diluted with 5 ounces of distilled water previously ascertained to be free from ammonia (an impurity not unfrequently met with in the first portions of water which come over in distillation); lastly, 50 grains of the mercurial test liquor are added.

If the tint coincides in intensity with that furnished by the distillate which has received an equal quantity of the mercurial test, the amount of ammonia may be considered to correspond with that taken in the liquid for comparison. If the distillate appear to have a deeper or a paler tint, a second approximative trial with a larger or a smaller quantity of sal-ammoniac must be made, and so on until the operator is satisfied that the tints coincide. On multiplying the number of grains of sal-ammoniac solution employed by 8, the product will give in 10,000ths of a grain the quantity of ammonia per gallon in the water under examination. Suppose that the observer estimates the amount of ammonia in the 125 c.c. on which he is operating, at 0·25 mgm., he takes 2·5 c.c. of the sal-ammoniac solution, and dilutes it with distilled water to 125 c.c.; he then adds 3 c.c. of the mercurial liquor, and compares it with the tint produced in the distillate by a like addition of the mercurial test. If the two tints correspond, multiply by 2 the number of c.c. of sal-ammoniac solution required, and the number obtained will give the proportion of ammonia per litre in tenths of a milligramme. When the quantity of ammonia exceeds the 20th of a grain per gallon, or 0·6 mgm. per litre, it is necessary to determine the amount by neutralisation.

Unless the amount of ammonia obtained by distillation alone, or with carbonate of soda be considerable (about 0·01 part in 100,000 parts of water) this modification of Nessler's process is all that could be desired for its accurate determination. But if a larger proportion than this be obtained in a potable water, the presence of urea may be suspected, and it becomes necessary to make the Nessler ammonia test directly in the original water without the intervention of distillation. For this purpose, however, the

water should be colourless, and free from calcic and magnesic carbonates. Any tint which is appreciable in a stratum 6 or 8 inches thick would obviously vitiate the result of a colour-test, whilst, if carbonates of calcium or magnesium be present, the addition of the Nessler solution will infallibly produce turbidity; moreover, we find that the slightest opalescence in the water, under these circumstances, is absolutely incompatible with an accurate determination. Both these difficulties may be effectually removed by adding to the water, first, a few drops either of perchloride of iron or chloride of aluminium in solution, and then a few drops of a solution of carbonate of soda, so as to precipitate sesquioxide of iron or alumina. The precipitate completely decolourises the water, and no turbidity is caused by the subsequent addition of the Nessler solution; but, unfortunately, the precipitate carries down with it an amount of ammonia which, in the case of the sesquioxide of iron, sometimes amounts to one-third of the total quantity present. Remembering the beautiful blue-green tint—the natural colour of absolutely pure water—which is presented by a reservoir of water that has been softened by Clark's process, Messrs. Frankland and Armstrong tried upon peaty water the effect of precipitating in it carbonate of lime, and found that the decolourisation was as complete as could be desired, and that no appreciable amount of ammonia was carried down with the precipitate. The amount of carbonate of lime present in a coloured water is rarely sufficient to enable the operator to carry out this reaction with sufficient rapidity and completeness; it is therefore best in all cases to add a few drops of a concentrated solution of chloride of calcium to half a litre of the water. The subsequent addition of a slight excess of carbonate of sodium then produces a copious precipitate of carbonate of calcium, which should be allowed to subside for half an hour before filtration. 100 c.c. of the filtrate is a convenient quantity to take for the direct Nessler determination of ammonia. To this volume of the filtrate 1 c.c. of the Nessler solution is added, and the colour observed as above described. By this direct process, the ammonia in fresh urine can be readily estimated; for this purpose 5 c.c. of the urine should be diluted with 95 c.c. of water free from ammonia. Known quantities of ammonia, added in the form of ammonic chloride to urine, can be determined with great accuracy.

The colour observations of the Nessler determination are best made in narrow glass cylinders, of such a diameter that 100 c.c. of the water to be tested form a stratum about 7 inches deep. The depth of tint is best observed by placing these cylinders upon a sheet of white paper near a window, and looking at the *surface* of the liquid obliquely.

Chloride of Ammonium in Analysis.—For the best method of removing the chloride of ammonium, which unavoidably accumulates in the process of analysis, see *ante*, p. 23.

CHAPTER II.

BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

Indirect Estimation of Barium, Strontium, and Calcium.

THE estimation of these three earthy metals is generally effected after they are separated from each other. These separations can be dispensed with if an indirect method be employed, thereby avoiding the loss attendant upon different separations, and materially hastening and simplifying the whole estimation. The following indirect method, which is very successful for the estimation of these three metals, may also be employed in the presence of magnesium.

In the first place, the calcium, strontium, and barium must be precipitated as carbonates, by means of carbonate of, and caustic, ammonia. It must be borne in mind that in a liquid containing much sal-ammoniac or nitrate of ammonium, neither calcium, strontium, nor barium can be completely precipitated by carbonate of ammonium; so that, after filtering, it is possible, by means of sulphuric acid or oxalate of ammonium, to recognise a more or less considerable quantity. The cause of this is, that ammoniacal salts of strong acids have a solvent action upon carbonate of calcium, and this action is still stronger upon the carbonates of strontium and barium. Should, on the other hand, acetate or carbonate of ammonium be used, instead of sal-ammoniac or nitrate of ammonium in solution, the precipitation of the three bases by carbonate of ammonium will be so complete that it will be impossible to discover in the filtrate, by means of the before-mentioned reagents, any traces of calcium, strontium, or barium.

In order to have in solution no other ammoniacal salts than acetate and carbonate of ammonium, it will suffice to add to the tolerably neutral solution as much acetate of sodium as there is supposed to be sal-ammoniac or nitrate of ammonium held in solution, and then to supersaturate with ammonia and carbonate of ammonium, and, after a short digestion, to cool the solution; the carbonated alkaline earths which have in this manner been completely precipitated are now filtered off.

Digestion is not absolutely necessary here; it only serves to render those deposits granular which would otherwise be voluminous. On the other

hand, in order to obtain complete precipitation, it will be necessary to reduce the whole to the ordinary temperature before filtering, because hot acetate of ammonium has a solvent action upon carbonated alkaline earths, although in a far less degree than sal-ammoniac.

A certain degree of dilution of the ammoniacal salt is to be recommended; in any case, the solution must not be more concentrated than in the proportion of one part of salt to twenty of water.

Carbonate of sodium may be substituted for the acetate, in order to decompose the sal-ammoniac; but if, at the same time, magnesium be held in solution, the presence of a large quantity of an ammonia salt of stronger acid than carbonic will be necessary, in order that it may not be deposited with the alkaline earths. For this purpose, the addition of acetate of sodium is eminently suitable, because the acetate of ammonium thus formed (as with oxygenated salts of ammonium generally) prevents the precipitation of the magnesium much more than sal-ammoniac does, without, as before remarked, dissolving barium, strontium, or calcium.

In the presence of magnesium, a too great excess of carbonate of ammonium must be avoided as a reagent, in order to hinder the formation of ammoniacal carbonate of magnesium, which is difficult to dissolve. After these precautionary measures, the barium, strontium, and calcium having been separated, the precipitate is washed, filtered, dried, heated, and weighed; it is then dissolved in a measured quantity of normal hydrochloric acid and estimated. This is done (after removing the carbonic acid by heat from the diluted solution, which is coloured with litmus) by estimating with normal standard ammonia solution the amount of hydrochloric acid which had been required to transform the three carbonates into chlorides. The solution is now mixed with bichromate of potassium and caustic ammonia in excess, to precipitate all the barium, so that no trace of it may be detected in the acidulated filtrate, by fluosilicate of potassium and alcohol.* The chromate of barium is filtered off and washed until acetate of lead ceases to give a yellow precipitate in the filtrate; to the solution chromic acid is now added, according to the usual process, together with a measured quantity of a standard solution of protosulphate of iron; and the amount of baryta is then obtained, according to the formula—

Chromic acid × 1527 = Baryta,

or Chromic acid × 1964 = Carbonate of Barium.

If, on the one hand, the amount of carbonate of barium thus obtained be deducted from the weight of the three carbonates, and, on the other, the

* Pure chloride of barium solution produces no turbidity when, after the precipitation of baryta by chromate of potash and ammonia, the filtrate is mixed with sulphuric acid. It is, of course, assumed that the reagents employed in precipitation are quite free from sulphuric acid.

amount of hydrochloric acid answering to the baryta be calculated, the difference between this amount of hydrochloric acid and the amount found, will be the quantity of hydrochloric acid which corresponds to the united weight of the carbonates of calcium and strontium, which has just been calculated.

The amount of carbonate of calcium and carbonate of strontium is obtained as follows:—Calculate the amount of carbonate of calcium (which is equivalent to the known quantity of hydrochloric acid) contained in the excess of carbonates of calcium and strontium; deduct this from the weight of the two carbonates, multiply the remainder by the constant factor $3\frac{1}{12}$, and the product will then be the required quantity of carbonate of strontium; this, when again subtracted from the united weight of both salts, yields, as its remainder, the quantity of carbonate of calcium. The constant factor, $3\frac{1}{12}$, is obtained by the following calculation:—

	Carbonate of calcium =	50
	Carbonate of strontium =	74
	Carbonates of calcium and strontium =	124
hence	2 eqs. of carbonate of calcium =	100

and this subtracted from the equivalent of carbonate of strontium leaves 24, and 74 divided by $24 = \frac{37}{12} = 3\frac{1}{12}$.

This method of estimating these three earthy metals always yields satisfactory results. It is quickly carried out, and is very exact, because the precipitations are all perfect, and the two volumetric estimations involved in the method admit of great accuracy. Moreover, the troublesome and somewhat uncertain separation of the strontium and calcium with a concentrated solution of sulphate of ammonium, which is very inconvenient in estimating the calcium, is avoided.

In the absence of strontium, either precipitate the calcium and barium as carbonates, estimating the precipitate alkalimetrically; or precipitate the barium as sulphate, and the calcium as carbonate, by digesting the solutions of both with a mixture of three parts of sulphate of potassium and one part of carbonate of potassium; weigh the dried and ignited precipitate, and estimate the carbonate of calcium alkalimetrically.

Estimation of Calcium.

Dr. A. Cossa has determined the accuracy of estimating calcium as quick-lime or caustic lime, instead of weighing it as carbonate of calcium. The experiments were made—(1) With pure oxalate of calcium previously dried at 100°; (2) with carbonate of calcium precipitated from a solution of pure chloride of calcium by means of pure carbonate of sodium; (3) with pure, native carbonate of calcium. The result of an average of three experiments with No. 1 is 0·07 per cent too low; with No. 2, 0·35 per cent too low; with No. 3, 0·27 per cent too high.

To avoid the inaccuracy and loss of time nearly always resulting from the ordinary method of determining calcium, viz., by strongly heating the precipitate of oxalate of calcium, and converting the same into carbonate by repeatedly moistening with solution of carbonate of ammonium, Mr. Scott recommends the weighing the precipitate as *sulphate* instead. The addition of sulphuric acid, or even of sulphate of ammonium alone, to caustic lime is hardly a safe operation, in an analytical point of view, if the mass in the crucible is at all bulky, but by using the following solution no inconvenience is experienced. Three parts of pure *liquor ammoniæ* of the ordinary strength should be just neutralised with pure sulphuric acid (previously diluted with its bulk of water), and two parts of the ammonia solution added. In each ounce of the fluid thus obtained 10 grains of chloride of ammonium must be dissolved; the whole may then be filtered into a small reagent bottle and appropriately labelled. It must, of course entirely volatilise when heated on platinum foil. In this manner the calcium is weighed as *sulphate* which may be strongly ignited without change, *one weighing* therefore being sufficient.

Phosphate of Calcium.

The commercial estimation of superphosphates is given in the chapter on "Phosphoric Acid." The following process, recommended by Professor F. Wöhler, for the analysis of apatite and similar phosphates, will be found to be one of the most trustworthy:—Dissolve the mineral in nitric acid in a capsule, and then add pure mercury in such a quantity that when the acid is saturated with it there still remains a portion of mercury undissolved. Evaporate the mixture on the water-bath to complete dryness. If a slight odour of nitric acid is still disengaged, add more water, and evaporate again to dryness, so as to get rid of it completely; then extract with water, place it on the smallest possible filter, and well wash the residue, which contains all the phosphoric acid.

Besides the excess of mercury the filtrate contains all the calcium. With hydrochloric acid precipitate the proto-salt of mercury. As a little binoxide of mercury may have been formed, precipitate the solution with ammonia. If the mineral contains iron or other bases precipitable with ammonia, these remain after calcining the last precipitate. The solution is rapidly filtered with as little exposure to the air as possible, and the calcium in it precipitated with oxalate of ammonium.

The filter, which, besides the excess of mercury, contains phosphoric acid, is well dried, and the whole is placed in a platinum crucible and mixed with carbonates of potassium and sodium. The crucible is then heated to a temperature below redness, under a chimney with a good draught, until all the mercury is volatilised, after which it may be heated to redness and

the contents fused. Then dissolve in water, add an excess of hydrochloric acid, and precipitate the phosphoric acid with ammonia and sulphate of magnesium.

To estimate the chlorine, dissolve a known weight of the mineral, in dilute nitric acid,* and precipitate the chlorine with nitrate of silver.

Some kinds of apatite contain a small quantity of fluorine. When it is desired to ascertain the presence of this body, finely powder the mineral, and then mix it in a platinum crucible with concentrated sulphuric acid; cover the crucible with a piece of glass, coated with wax, and having characters traced on it with the point of a needle. Then heat the crucible, taking care not to melt the wax. If fluorine is present, the characters will be found engraved on the glass when the wax is removed. The amount of fluorine present may be deduced from the loss of weight obtained in the complete analysis.

Separation of Strontium from Barium.

When in the form of sulphates, prolonged digestion with a cold solution of carbonate of ammonium will convert the strontium into carbonate, whilst it has no action on the barium. Boiling the solution, or employing carbonate of sodium, is not so effectual. Finely pulverise the mixed salts, wash thoroughly with water, and treat with nitric acid. The strontium will dissolve as nitrate and leave the residue of the sulphate of barium. Barium and calcium may be separated in a similar manner.

Separation of Strontium from Calcium.

The best process is that originally devised by Stromeyer, based upon the solubility of nitrate of calcium in absolute alcohol and the insolubility therein of nitrate of strontium, but adding an equal volume of ether to the alcohol. A mixture of alcohol and ether does not dissolve more than 1-60,000th part of nitrate of strontium, whilst it dissolves nitrate of calcium perfectly.

A similar separation may be effected by sulphate of ammonium, in which sulphate of calcium is soluble, whilst sulphate of strontium remains unaffected. The proportions to employ are, 50 parts of sulphate of ammonium and 200 parts of water to 1 of sulphate of strontium. There is then formed a soluble double salt, which resembles potassio-gypsite (sulphate of calcium and potassium). This process is, however, less delicate than that of Stromeyer.

Calcium, Detection of in the Presence of Strontium and Barium.

An ammoniacal solution of arsenious acid gives a precipitate of arsenite of calcium in neutral calcium salts. Under similar circumstances barium and strontium give no precipitate.

* Certain brown apatites leave as a residue a small quantity of a crystalline powder, which is cryptolite (phosphate of protoxide of cerium).

MAGNESIUM.

Applications of Metallic Magnesium.—The magnesium which is now met with in commerce in the form of ribbon, wire, and rod, possesses properties which render it of great value in some chemical operations.

When magnesium is added to a slightly acid solution of iron, zinc, cobalt, or nickel salts, an evolution of hydrogen takes place, and these metals are respectively precipitated in the metallic state. When washed, dried, and compressed, the precipitated metals possess great brilliancy and dissolve completely in acids. The iron, cobalt, and nickel so obtained are highly magnetic. Besides these metals, magnesium precipitates gold, silver, platinum, bismuth, tin, mercury, copper, lead, cadmium, and thallium.

When magnesium is put into water containing a little common salt, sal-ammoniac, or dilute acid, very pure and inodorous hydrogen gas is evolved. Owing to the high electro-motive power of magnesium, and its low equivalent, it would be decidedly the best positive element for galvanic batteries could it be produced at a cheap rate.

When magnesium is introduced into an acid solution containing arsenic or antimony, these metals are not precipitated, but combine with the evolved hydrogen, and pass off as arseniuretted or antimoniuretted hydrogen. Owing to the great purity of the distilled magnesium of commerce, and its freedom from silicium and poisonous metals, it is invaluable to the toxicologist, and should always be used in Marsh's apparatus instead of zinc, for the evolution of hydrogen. Further particulars as to the special employment of magnesium for this purpose will be found in the chapter treating on Arsenic.

Calcium and Magnesium, Separation of.

The method of separating calcium and magnesium by means of oxalate of ammonium does not succeed when only a very small quantity of calcium is present. In such a case the calcium is either not precipitated at all or but very incompletely. Free ammonia also tends to hinder the precipitation, and, when it has evaporated, crystals are obtained, which consist of oxalate of calcium with oxalate of magnesium, and the liquid still contains calcium. A better result, Scheerer says, is obtained by converting the alkaline earths into neutral sulphates, and adding alcohol to the aqueous solution until a persistent cloudiness is produced. After some hours all the sulphate of calcium is deposited. When too much alcohol has been used, some of the sulphate of magnesium is deposited as well; it is sufficient then to re-dissolve the sulphates in water and precipitate a second time with alcohol, or the calcium may now be thrown down by the oxalate of ammonium. The magnesium not being in excess, no longer hinders the precipitation.

As regards the analysis of dolomite, Dr. A. Cossa states, that when care is not taken to re-dissolve the precipitate of oxalate of calcium first obtained, and re-precipitate this a second time, it is always so contaminated with oxalate of magnesium or ammonio-oxalate of magnesium that the quantity of calcium found as carbonate may be 0·62 per cent in excess of what it ought to be, while the loss for carbonate of magnesium may even be as high as 0·78 per cent.

When, in the ordinary course of qualitative analysis, carbonate of ammonium is used to separate calcium from magnesium, unless the former metal is present in notable proportion to the latter, a very insoluble double carbonate of magnesium and ammonium always accompanies the carbonate of calcium, if this is allowed sufficient time to form. If much magnesium and no calcium be present, the magnesium precipitate still falls after awhile. Both metals are precipitated by this reagent, the only difference being that the calcium precipitate forms somewhat earlier than the magnesium precipitate. Calcium, therefore, can only be separated from magnesium by this reagent by fractional precipitation, which necessarily involves loss of substance; and, in qualitative examination, the method is sure to mislead when the proportion of calcium present is small, unless it is controlled by other methods. The same remarks apply, in substance, to the method of precipitation by oxalate of ammonium. Within a trace the whole of the magnesium present in a considerable quantity of solution of chloride of magnesium can be precipitated simply by successive additions of oxalate of ammonium—the solution being concentrated to its original bulk after the last addition of the reagent. Yet, in working with this reagent, the rule is, that enough of it must always be added to transform all the magnesium salt into oxalate, since oxalate of calcium is soluble in solution of chloride of magnesium. That some magnesium salt must precipitate with the calcium salt under such conditions is obvious; and that it does so is well known, and is, though incompletely, provided for by the direction being given to repeat the process upon the precipitate first obtained. This process, therefore, is also one of fractional precipitation, and for it to approach success, the operator must know pretty nearly beforehand how much calcium, in proportion to the magnesium present, he has to deal with.

Mr. Edward Sonstadt has discovered that in common tungstate of sodium we possess a test for calcium which is probably equal in delicacy and in certainty to that of chlorine for silver, or of sulphuric acid for barium, and on this discovery he has based an excellent method for the separation of magnesium from calcium.

Mr. Sonstadt gives the following details, respecting the manipulation required in separating calcium from magnesium by tungstate of sodium, that experience has shown to be necessary. It is convenient to have the

solution of the magnesium and calcium salts made somewhat alkaline by ammonia, but a very large quantity of this, as well as of ammoniacal salt, is to be avoided. The beaker in which the precipitation is to be effected should, while perfectly dry and warm, be rubbed within by chamois leather on which a drop or two of fine oil (such as is used for oiling balances) has been put. If this precaution be not taken, it will be found impossible to detach the precipitate of tungstate of calcium from the sides and bottom of the vessel. A considerable excess of the reagent is not necessary; but, if it occur, is not material. If, on addition of the reagent, a white, flocculent precipitate forms immediately, it is well to add a few drops of ammonia, when the flocculent precipitate will re-dissolve; but if it does not re-dissolve, after warming, there is some other element present, which, if ordinary Epsom salts are used, will probably be manganese. The tungstate of calcium precipitate is very dense; it forms slowly in very dilute solutions, and, in all cases, several hours should be allowed for it to form. The solution should be warmed meanwhile, but must not be allowed to boil. The precipitate must be washed till the filtrate shows no cloudiness on standing, with nitrate of silver when the salts are chlorides; or, if they are sulphates, till chloride of barium gives no cloudiness. The precipitate must then be further washed with dilute solution of ammonia, but these washings need not be saved. The filter should be burnt separately, after the precipitate is cleared from it as nearly as possible. After the ignited precipitate is weighed, a little strong solution of ammonia should be poured upon it, and allowed to stand for a while, when the ammonia is decanted, and supersaturated with acid. If a precipitate falls after a time, the tungstate of calcium precipitate should (without being removed from the crucible) be allowed to stand for some hours with more ammonia; it is then washed by decantation, again ignited, and weighed. The ignited precipitate should be perfectly white.

The filtrate, containing the magnesium salt and tungstate of sodium, may be at once precipitated by phosphate of sodium in the usual way; but if this is done, much washing is required to get rid of the little tungstic acid that adheres obstinately to the precipitate. It is better, especially when a great excess of the reagent has been used, to first precipitate the tungstic acid by a considerable excess of hydrochloric acid, and boil until the precipitate becomes dense and intensely yellow. The solution is then filtered, supersaturated with ammonia, and the magnesium precipitated in the usual way; but, even in this case, it is better to wash lastly with stronger ammonia solution than ordinary.

Separation of Magnesium from Potassium and Sodium.

In the following method phosphoric acid can be employed under all circumstances, since its ill effects are neutralised by the complete elimination of any excess of it.

Acidulate the liquid with nitric acid, and then add excess of ammonia. To the filtered liquid add phosphate of ammonium, or simply phosphoric acid, and collect the ammonio-magnesium phosphate precipitate. To get rid of the ammoniacal salts, filter, evaporate, and calcine; this causes the greater part, or even the whole, of the hydrochloric acid to be eliminated, when that acid is present, and the two bases remain united with phosphoric acid only. However, to make certain, treat the residue two or three times with concentrated nitric acid and calcine, when the whole of the hydrochloric acid being thus eliminated, only phosphoric acid, potash, and soda remain. The residue is collected in a flask and treated by a large excess of tin and nitric acid; the phosphoric acid being thus rendered insoluble, the liquid is filtered and concentrated. The residue, composed of nitrates of potassium and sodium, is calcined till completely decomposed, and as soon as the capsule is cooled the caustic alkalies are transformed into carbonates, after which they are converted into chlorides, then into sulphates, and finally carbonate of ammonium is added to decompose the bisulphate of potassium. With these combined elements it is possible to determine the quantity of each alkali indirectly.

The exactness of this process consists in the method of removing the phosphoric acid,—a method founded on the property (discovered by A. Reynoso) possessed by stannic acid of forming a combination with phosphoric acid completely insoluble in water and in nitric acid. To render this process accurate, the hydrochloric acid must be eliminated,—an object easily effected.

CHAPTER III.

CERIUM, LANTHANUM, DIDYMIUM, GLUCINUM, YTTRIUM, TITANIUM, ZIRCONIUM.

CERIUM, LANTHANUM, AND DIDYMIUM.

Separation and Estimation of the Three Cerium Metals together.

THE precipitation of the cerium metals in the form of oxalates from a slightly acid solution is, unquestionably, the most satisfactory method of separating these oxides. The estimation of the oxalates upon a weighed filter is accompanied with the usual trouble and loss of time in perfectly drying the filter before and after collecting the precipitate upon it. By the following mode of proceeding Dr. W. Gibbs completely avoids these difficulties. The usual mixture of cerium, lanthanum, and didymium, when neutral, is to be rendered slightly acid by sulphuric or hydrochloric acid, and then largely diluted with water. Half a litre of water for every estimated gramme of oxide is a good working proportion. The solution is then to be boiled, and a hot solution of oxalic acid or oxalate of ammonium added. On cooling, especially when the solution has been well stirred with a glass rod, or shaken, the oxalates separate in large crystalline grains of a pale rose violet colour. The precipitate is to be filtered off and well washed with boiling water, the washing being extremely easy in consequence of the coarse granular character of the precipitate. The filter is then to be pierced and the oxalates carefully washed down into a crucible; after which the water in the crucible may easily be removed by evaporation, and the oxalates dried at a temperature of 100°. The equivalents of lanthanum and didymium are so near to that of cerium, that no very sensible error is committed by considering the mixed oxalates as consisting simply of oxalate of cerium with three equivalents of water.

Separation of Cerium from Didymium and Lanthanum.

The following method, which we owe to the researches of Messrs. Pattison and Clarke, has been found to be very effective for the separation of cerium from didymium and lanthanum:—It is based upon the fact that when chromate of cerium is evaporated to dryness and heated to about 110°, it is decom-

posed, and the oxide of cerium remains as an insoluble powder, whilst the chromates of didymium and lanthanum, when subjected to the same treatment, remain unchanged.

The mixed oxides of cerium, didymium, and lanthanum are subjected to the action of aqueous solution of chromic acid, aided by heat till solution is complete. The chromic acid need not be entirely free from sulphuric acid. The solution obtained is evaporated to dryness, and the residue heated to about 110°. Hot water is then added, which dissolves the lanthanum and didymium and leaves the oxide of cerium, which is then separated by filtering. Thus obtained, the oxide of cerium is a yellowish-white powder which is almost completely insoluble in acids, but is rendered soluble by fusion with the acid sulphate of potassium.

This process may also be employed for the quantitative determination of cerium, as it has been found, by careful trial, that not a trace of cerium can be detected by the best known processes in the solution, after its separation as above described.

Dr. Wolcott Gibbs has found that when a salt of cerium, lanthanum, and didymium is boiled with dilute nitric acid, and peroxide of lead added to the solution, the cerium is quickly, and under some circumstances completely, oxidised, the solution becoming more or less deeply orange-yellow. This process affords an extremely simple and delicate test for cerium ; it succeeds with all the salts which are soluble in nitric acid, though, of course, when the mixed oxalates are tested the oxalic acid is oxidised to carbonic acid before the characteristic cerium yellow appears. For the purpose of testing it is sufficient to dissolve the salt to be examined in nitric acid diluted with its own volume of water, to add a small quantity of pure peroxide of lead, and boil for a few minutes, when the smallest trace of cerium can be detected by the yellow colour of the solution. When a solution containing a salt of cerium dissolved in strong nitric acid is boiled for a short time with a large excess of peroxide of lead, oxygen gas is copiously evolved, and, at the same time, the sesquioxide of cerium formed at first is completely reduced to protoxide, the solution becoming perfectly colourless. The remarkable reaction which occurs in this case appears to be connected with the formation of nitrate of lead, since, when the solution of protoxide of cerium contains a large excess of this salt, the cerium is not peroxidised by boiling with nitric acid and the peroxide.

When a solution of cerium, didymium, and lanthanum is treated with nitric acid and peroxide of lead in the manner pointed out above, the deep orange-coloured liquid evaporated to dryness, and heated for a short time to a temperature sufficiently high to expel a portion of the acid, it will be found that boiling water acidulated with nitric acid dissolves only the salts of lanthanum and didymium, leaving the whole of the cerium in the form of

basic nitrate insoluble in water. The insoluble matter is to be filtered off and thoroughly washed. A current of sulphuretted hydrogen passed into the filtrate removes the lead, after which the lanthanum and didymium may be precipitated together as oxalates, which, if the process has been carefully performed, are perfectly free from cerium. The mass on the filter is readily dissolved by fuming nitric acid. Sulphuretted hydrogen is then to be passed through the solution, sufficiently diluted with water, until the lead is completely precipitated. The cerium may then be thrown down by oxalic acid, ignited, and weighed as ceroso-ceric oxide or converted into sulphate and weighed as such.

Nitrate of protoxide of cerium obtained by this process gives, when tested by the spectroscope with transmitted light, even in very thick layers, a scarcely perceptible indication of didymium.

Another very good method of separating the cerium from lanthanum and didymium is to precipitate the three metals in the state of gelatinous hydrates by adding an excess of caustic potash to their solution. These oxides are washed several times by decantation, and then a concentrated solution of caustic potash added, and the whole submitted to a current of chlorine. The alkaline liquid being thus saturated with chlorine, the oxides of lanthanum and didymium are re-dissolved, lemon-coloured insoluble ceric oxide remaining. This substance is washed on a filter, then re-dissolved, while still moist, in hydrochloric acid, precipitated by oxalate of ammonium, and strongly calcined; the cerous oxalate is thus transformed into very light rose-coloured ceroso-ceric oxide.

The chlorinated liquid contains oxides of lanthanum and didymium, which may be precipitated together by adding oxalate of ammonium.

Separation of Lanthanum and Didymium.

The nitric acid solution of lanthanum and didymium is evaporated to dryness in a flat-bottomed capsule. The dried mass is of a pale rose tint. By exposing the capsule for a few minutes to a temperature of 400° or 500°, the saline mass will be fused, with disengagement of nitrous vapours. The capsule is withdrawn from the fire before the decomposition is complete, and hot water must be poured in. Part of the matter dissolves and part remains insoluble in the form of greyish-white flakes (with no nitrate of didymium). The whole is left to stand for a few hours, then boiled and filtered; if the liquid still retains a feeble rose tint, the same operation must be repeated until a colourless liquid is obtained, containing nitrate of lanthanum, free from subnitrate of didymium. Oxide of lanthanum is obtained by evaporating this liquid and strongly calcining the residue. The oxide of didymium may also be estimated after the calcination of the subnitrate thus obtained.

This process, which was first devised by MM. Damour and Deville, is founded on the fact that nitrate of didymium decomposes before nitrate of lanthanum, and that the first of these salts changes to the state of sub-nitrate. Several precautions must be observed. The bottom of the capsule containing the mixture of the two salts must not be too much heated, nor must too large quantities of material be used, as in that case it forms a thick layer at the bottom of the capsule and decomposes unequally. It is better to re-commence the operation several times than to heat too strongly in attempting to separate the two oxides at the same time. The first portions of oxide of didymium obtained in this way give, with sulphuric acid, reddish-violet crystals, with traces of white needle-shaped ones, which seem to belong to the sulphate of lanthanum. The last portions give a sulphate less coloured, but, like the preceding, with the same crystalline form derived from the oblique rhomboidal prisms; the needles of sulphate of lanthanum are rather more numerous. Finally, the above-described colourless solution gives, with sulphuric acid, colourless crystals derived from the right rhomboidal prism, characteristic of sulphate of lanthanum.

By following this method, the estimation of didymium comes out rather too high, and, consequently, that of lanthanum rather too low.

Dr. C. Winckler has ascertained that when cerium is separated from its solutions by binoxide of mercury and permanganate of potassium the cerium is not merely precipitated in the state of a peroxide, but is accompanied by didymium, whilst the lanthanum remains in solution. This is an excellent method for separating didymium from lanthanum. To obtain the didymium which accompanies the cerium in its precipitation by permanganate of potassium, re-dissolve the precipitate in hydrochloric acid. After having well calcined it to free it from the oxide of mercury, evaporate the hydrochloric solution to dryness in the presence of sulphuric acid; dissolve the residue of sulphate in water, and add sulphate of potassium to it. In twenty-four hours a triple sulphate of cerium, didymium, and potassium separates, insoluble in sulphate of potassium.

The precipitate must then be dissolved in water, and the sulphates changed to oxalates, which are calcined to obtain the oxides of cerium and didymium; these are then separated in the usual way.

The lanthanum in the filtered liquid may be obtained thus:—First treat the filtered liquid with sulphuretted hydrogen, to separate the oxide of mercury, then precipitate the lanthanum as an oxalate, and calcine it. The oxide of lanthanum then contains very little didymium.

Lanthanum and didymium may also be separated by taking advantage of the different solubilities of their sulphates. By digesting a mixture of the dry salts in cold water (5°), a saturated solution may be obtained, which, upon being heated to 30° deposits sulphate of lanthanum, whilst sulphate

of didymium remains dissolved. The salts may be obtained quite pure by repeating this operation two or three times. Sulphate of lanthanum is colourless, whilst sulphate of didymium is of a beautiful rose-red.

GLUCINUM.

Preparation of Pure Glucina.

The simplest way to prepare a chemically pure salt of glucina is to make use of the process devised by Dr. W. Gibbs. The crude glucina obtained in the ordinary manner from beryl, but still contaminated with alumina, iron, &c., is fused with twice its weight of fluorhydrate of fluoride of potassium, and the fused mass treated with boiling water, to which a small quantity of fluorhydric acid has been added. On filtering, a notable quantity of the insoluble fluoride of aluminium and potassium almost always remains upon the filter, even when the separation of glucina has been carefully executed by means of carbonate of ammonium. The filtrate, on cooling, deposits colourless transparent crusts of the double fluoride of glucinum and potassium, which are easily purified by re-crystallisation.

Glucina may be prepared direct from beryl by this process, but as beryl only contains 13 or 14 per cent of glucinum, it will be more economical to separate the other oxides, as far as possible, by the ordinary methods, and then to purify the crude glucina by the above process.

From the aqueous solution of the double fluoride, pure glucina may be precipitated directly by ammonia.

Separation of Glucinum from the Cerium Metals.

The separation may best be effected in the following way:—Convert the salts into sulphates, and dissolve in the smallest quantity of water. If iron be present, reduce it to the state of protosulphate, by passing a stream of sulphuretted hydrogen through the hot solution; if this precaution is not taken, the precipitated double sulphates will contain iron. Then add a saturated solution of sulphate of sodium (which Dr. W. Gibbs has shown to be greatly superior to sulphate of potassium for this purpose), and sufficient of dry sulphate of sodium in powder to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sulphates of sodium and the cerium metals separate immediately as a white, highly crystalline powder, which is thrown upon a filter and washed thoroughly with a hot saturated solution of sulphate of sodium. After washing, the double sulphates on the filter are to be dissolved in hot dilute hydrochloric acid, the solution largely diluted with water, and the cerium metals precipitated by oxalate of ammonium. From the filtrate the

glucinum may be precipitated at once by oxalate of ammonium, after peroxidising the iron (if present) by means of chlorine water, and slightly acidulating with sulphuric acid.

YTTRIUM.

Separation of the Yttrium Metals from Glucinum.

These metals may be separated by mixing the precipitated hydrated oxides with sugar, drying, and then heating to redness in a covered crucible. The black carbonised mass is then introduced into a piece of combustion-tubing, and heated to redness, whilst a slow current of dry chlorine is passed over. The chlorides of the yttrium metals are non-volatile, whilst chloride of glucinum volatilises and may be collected in any appropriate condenser.

Separation of the Metals of Yttrium from those of Cerium.

The yttrium metals behave the same as glucinum, in respect to sulphate of sodium. The double sulphates of sodium and the yttrium metals, being readily soluble in sulphate of sodium solution, may be separated from cerium, lanthanum, and didymium in the way detailed on p. 45.

TITANIUM.

Preparation of Pure Titanic Acid.

The best plan for preparing pure titanic acid is Wöhler's; it is as follows:—Fuse the rutile or titaniferous iron with an excess of carbonate of potassium at a high temperature, in a fire-clay crucible. Pour the fused mass out into a piece of sheet-iron, so as to form, on cooling, a thin cake; next, grind this to powder, thoroughly exhaust with water, which leaves the greater part of the iron undissolved, and saturate the filtrate with hydrofluoric acid. A formation of fluotitanate of potassium soon occurs in white scaly crystals resembling boracic acid. These may be rendered quite free from iron and silicium by a few crystallisations from hot water, and ammonia will then precipitate pure titanic acid from their hot aqueous solution.

Another method for the preparation of pure titanic is to fuse the rutile or titaniferous iron with carbonate of potassium, and exhaust the fused mass with water in the manner above described. After filtering from the insoluble portion, the liquid is slightly supersaturated with hydrochloric acid added in the cold; it is then filtered if necessary. Acetic acid and dilute sulphuric acid are now added, and a brisk current of steam is passed in for several hours, the liquid being kept boiling all the time. Pure titanic acid will be precipitated.

ZIRCONIUM.

Preparation of Pure Zirconia.

The zircon or jargon is first broken up in a diamond mortar, and next reduced to an impalpable powder in an agate mortar. It is then mixed with fluorhydrate of fluoride of potassium, and the mixture fused. In this manner a perfect resolution of the mineral is easily obtained. The fluozirconate of potassium is then dissolved out from the insoluble fluosilicate by means of hot water acidulated with hydrofluoric acid. From this solution zirconia may be precipitated by ammonia.

In Messrs. Tessié du Motay and Co's. patent for improvements in preparing zirconia for purposes of oxyhydrogen illumination, the following process is given. The zirconia is extracted from its native ores by transforming, by the action of chlorine, in the presence of charcoal, the silicate of zirconium into double chloride of zirconium and of silicium. The chloride of silicium, which is more volatile than the chloride of zirconium, is separated from the latter by the action of heat; the chloride of zirconium remaining is afterwards converted to the state of oxide by any of the methods now used in chemistry. The zirconia thus obtained is first calcined, then moistened, and submitted in moulds to the action of a press with or without the intervention of agglutinant substances, such as borax, boracic acid, or clay. The sticks, cylinders, discs, or other forms thus agglomerated, are brought to a high temperature, and thus receive a kind of tempering or preparing, the effect of which is to increase their density and molecular compactness.

Of all the known earthy oxides zirconia is the only one which remains entirely unaltered when submitted to the action of a blowpipe fed by oxygen and hydrogen. Zirconia is also, of all these earthy oxides, that which, when introduced into an oxyhydrogen flame, developes the most intense and the most fixed light.

It has long been suspected that zirconia really consisted of a mixture of two or more closely allied oxides. In 1845 Svanberg announced that the zirconia contained in the various zircons from Siberia, Norway, and Ceylon, as, also, in the hyacinths from Espailly and Ceylon, was a compound of two or more earths, one of which he termed noria; and in a subsequent paper the same author also found this to be the case with the earth in the Greenland eudialite. His arguments—for he did not succeed in separating the earths—were founded upon his observations that the salts of zirconium did not always contain the same constant proportion of acid to base; that the oxalates, chlorides, and sulphates differed in their behaviour and solubility in certain reagents, and that the specific gravities of the natural silicates (zircon) from various localities differed greatly from one

another. These observations of Svanberg, notwithstanding the promise contained in his short paper on the subject to bring forward fuller evidence, have, as yet, never been followed up by him, and the subsequent researches of other chemists appear to throw doubt as to their correctness in several points, as well as to render the existence of his noria extremely dubious. The researches of Berlin (*Journ. f. Prakt. Chemie*, lviii., p. 145, 1853) showed that the results of the fractional precipitation of chloride of zirconium by oxalic acid did not warrant the conclusions of Svanberg, and that the zirconia prepared from zircons from Frederiksvaern, Espailly, Ural, India, and from the Ceylon hyacinths and Norwegian katapleeite, behaved in similar manner with oxalic acid, and that their oxalates were easily and completely soluble in excess of that acid, and that the specific gravity and amount of zirconia obtained from the oxalates from Frederiksvaern zircon and katapleeite which he examined were identical, so that it would seem necessary to seek for some other means of separating the earths than by the employment of oxalic acid.'

In 1864, Nylander, in a paper, "Bidrag til Kännedomen om Zirkonjord" (*Acta Universitatis Lundensis*, 1864), has examined the zirconia from the Norwegian eucolite, and considers that it contains two earths, which differ in their behaviour and solubility of their double potassium sulphate salts, but he also appears to have come to no definite results as to the existence or isolation of the earths themselves.

In 1869, Mr. David Forbes, F.R.S., was induced, on the representation of Mr. Sorby that certain specimens of the oriental jargon probably contained a considerable amount of an earthy oxide different from zirconia, to examine chemically one of the jargons forwarded to him by Mr. Sorby. As the means employed appear to throw some light on the characters of the earth hitherto regarded as zirconia, the following extracts are given from Mr. Forbes's paper which appeared in the "Chemical News" for June 11th, 1869 (vol. xix., p. 277):—

"The fragments, which were extremely hard, were broken up in a diamond mortar, previous to being reduced to as impalpably fine a powder as possible in an agate mortar; 16·22 grains of this powder were then thoroughly mixed with 81 grains pure anhydrous carbonate of sodium, placed in a platinum crucible, and fused at the highest heat of a large air gas blowpipe jet, after having been previously kept for two hours over a powerful Bunsen's flame, so as to "frit" it, or ensure combination previous to fusion. After complete fusion, a small lump of pure hydrate of sodium (about 15 grains) was, as recommended by Berzelius, carefully deposited in the centre of the fused mass, and a second similar piece added after the first had been absorbed; the fused substance became much more liquid after this addition; the heat was kept up for another half hour longer, and the

whole was allowed to cool. By the above means the mineral was perfectly decomposed, and the silica so altogether transferred to the sodium that it could be completely removed by cold water, leaving no trace behind with the earths. Previous experience with the zircons from various localities, and hyacinths from Ceylon, had proved that the perfect decomposition of these minerals is often attended with considerable difficulty. The fused mass when cold was treated repeatedly with cold water in a silver vessel, decanting off the supernatant solution each time, until the silica was entirely removed, and a white powder, probably a compound of the earth with soda, remained behind. The solution, which contained all the silica, was acidified with hydrochloric acid, evaporated to dryness, and the silica determined as usual. The silica obtained weighed 5·45 grains, consequently was equivalent to 33·61 per cent in the mineral.

"The white insoluble residue previously mentioned was found to be perfectly soluble in hydrochloric acid; in order to test if it contained any silica, the solution was evaporated to dryness and re-dissolved in water acidulated by HCl, but left no trace of insoluble matter behind. From the colour of the solution being distinctly yellow, it evidently contained oxide of iron, which I had scarcely expected, since the original mineral was nearly, if not altogether, devoid of colour; the solution, consequently, was a chloride of the earths of the jargon, accompanied by some sesquichloride of iron.

"Berzelius many years ago devised a means of separating oxide of iron from zirconia, founded upon the behaviour of their respective chlorides, the sesquichloride of iron being soluble in strong hydrochloric acid, whilst that of zirconia is nearly insoluble; I had tried this process previously with zirconia from Ceylon hyacinths, and had not been satisfied with it, as the iron solution carried along with it a not inconsiderable portion of the earth. It now struck me, however, that possibly the earth so dissolved might differ in character from that contained in the insoluble chloride, and I therefore determined to make the experiment.

"The hydrochloric acid solution was consequently again evaporated until it solidified as a yellow saline mass, whereupon it was treated repeatedly with cold strong hydrochloric acid of density 1·138, allowing it to stand some time, and decanting the solution as long as the fresh acid acquired the faintest yellow tinge. A yellow solution was obtained, leaving behind a snow-white chloride, crystalline in appearance, and completely soluble in water, forming a perfectly colourless solution. From this solution ammonia precipitated a flocky, but apparently rather dense, white precipitate, which, after being thoroughly washed, dried, and ignited, was of a pure white colour, and possessed a peculiar waxy look and dense appearance; it weighed 7·48 grains, and consequently amounted to 46·12 per cent of the jargon examined." This earth appeared to be pure zirconia.

"The yellow hydrochloric acid solution was now examined, and found, besides sesquioxide of iron, to contain a considerable amount of an earthy base, like zirconia. I decided to separate the iron by the tartaric acid and sulphide of ammonium process recommended by Berzelius, and, consequently, the solution was first supersaturated by ammonia, which threw down a faint yellowish white, somewhat flocculent precipitate. Tartaric acid, in excess, was then added, which dissolved at once the greater part of the precipitate, but, notwithstanding that a very large excess was added, a portion of the precipitate refused obstinately to re-dissolve, even upon application of heat. In order to examine this, the solution was filtered: a white, flocculent, and somewhat glutinous substance was left upon the filter, which, when well washed with hot water, dried, and ignited, weighed 1·24 grains, equivalent to 7·64 per cent of the original mineral.

"This body, after ignition, appeared very different from the previously-obtained zirconia; it was a white powder, but did not aggregate together or form lumps having a waxy lustre on the surfaces of fracture; on the contrary, it was more pulverulent, had a dead white, or mealy, appearance, and did not appear to be of any great density.

"Ammonia was now added in excess to the tartaric acid solution, which remained clear. Upon the further addition of sulphide of ammonium, the solution assumed a dark brown colouration; but no precipitate separated before the lapse of some days, when a black deposit of sulphide of iron formed, which was collected upon a filter, after the greater part of the supernatant liquid had been carefully syphoned off. This sulphide of iron was converted into sesquioxide, and afforded 0·04 grain, equivalent to 0·24 per cent in the mineral. After separation of the iron, the solution was evaporated to dryness in a platinum capsule, and ignited for some time, to drive off all ammoniacal salts, and oxidise the carbon resulting from the decomposition of the tartaric acid. There then remained behind an earthy body, of a white colour, having a slight tinge of grey, which weighed 2·03 grains, or 12·52 per cent. In appearance, this earth was quite different from the zirconia, and more resembled the second earth obtained. Possibly this substance may contain a third earth analogous to zirconia, such as Svanberg (*Ofversigt. Kongl. Vet. Acad.*, pp. 34, 37, 1845) suggested was present in eudialite and certain zircons.

"The result of this examination of the jargon, when summed up, indicates its composition to be as follows:—

	In 16·22 grains.		In percentage.	
Silica	5·45		33·61	
Zirconia α	7·48		46·12	
" β	1·24	10·75	7·64	66·28
" γ	2·03		12·52	
Sesquioxide of iron	0·04		0·24	
	16·24		100·13	

"The formula ZrO_2SiO_2 ascribed to zircon requires—

Silicic acid	33·77
Zirconia	66·23
	100·00

with which the numbers found for jargon are closely approximative."

The results of this chemical examination must be considered as strengthening the evidence, physical and chemical, that the earth usually denominated zirconia is, in reality, a compound of two, if not more, closely allied oxides.

Separation of Zirconium from Titanium.

This separation is one of the most difficult problems in analytical chemistry. Titanic acid and zirconia, which separately may be estimated with the greatest accuracy, when together present such properties that it might be said one of these two bodies had partly destroyed the individuality of the other, since the reactions they possess when separate they no longer possess together, whilst in some cases they act quite differently. Thus, it is well known that titanic acid in the state of sulphate is completely precipitated by boiling in a diluted solution; but that when in presence of zirconia there may be, according to the proportions of the two bodies, either incomplete precipitation or none at all. Moreover, the precipitated titanic acid always retains zirconia, although the greater part remains in solution with the rest of the titanium.

Messrs. G. Streit and B. Franz say that when titanic acid is precipitated from a solution containing zirconia, by boiling with dilute sulphuric and acetic acids, the precipitated titanic acid is free from zirconia. The boiling should be performed by the aid of steam, and be continued for eight or ten hours. They experimented with a solution containing 4·23 grms. of TiO_2, and added thereto the sulphuric acid solution of 0·613 grm. of zirconia. To the solution was then added its own bulk of acetic acid, and the liquid boiled; all the titanic acid was thereby precipitated, while zirconia remained in solution. From the filtrate the latter substance was precipitated by ammonia, and, after having been collected upon a filter, washed, dried, ignited, and weighed. The quantity obtained was very near the amount required by theory.

F. Pisani adds metallic zinc to a mixed solution of titanic acid and zirconia in sulphuric or hydrochloric acid, until the titanium is reduced to the state of sesquioxide of titanium, giving the liquid a more or less intense violet colour. Titanic acid and zirconia are precipitated equally by sulphate of potassium; but if the titanium is previously reduced in this manner only the zirconia is precipitated. Add excess of sulphate of potassium to the violet

liquid, which should be small in quantity and not too acid, the zinc being still slowly attacked; leave the whole to stand for some time, then filter quickly and wash the precipitate with a solution of sulphate of potassium; afterwards extract the zirconia by the usual processes. Upon dissolving this zirconia in hydrochloric acid, and reducing by zinc, it will be found that only a trace of titanium remains.

Unfortunately, this process is not quite accurate, and cannot be used for quantitative separation.

Titanic acid may, however, be estimated quantitatively in the presence of zirconia, by volumetric means. The above described violet solution of sesquioxide of titanium is a powerful reducing agent. On pouring permanganate of potassium in this liquid, titanic acid is formed, and the solution gradually loses its colour, until it becomes rose. According to the quantity of permanganate of potassium it is found necessary to add, may be calculated the quantity of titanic acid, taking for each equivalent of iron to which the permanganate corresponds, one equivalent of titanic acid. The following is the mode of operating as described by Pisani, to whom this process is due:—

Titanic acid in solution in hydrochloric acid is best, because, if in the state of sulphate, it is liable to be partially precipitated by the rising of the temperature before its complete reduction has been effected. The reduction should be effected in a flask, to which has been adapted a cork with a tube drawn out to a point, so as to keep the liquid from contact with the air. The quantity of liquid should not be great, and should be acidified until the disengagement of hydrogen becomes regular; then heat gently to accelerate the reduction, and when the colour of the liquid ceases to increase in intensity, leave it to get quite cold, and dilute the liquid with cold water which has been previously boiled to free it from air, as it would otherwise oxidise the titanium. As soon as the liquid is diluted, decant it into a glass without taking the zinc with it, wash the flask once or twice, and then rapidly pour in the permanganate of potassium. The combined weight of titanic acid and zirconia being previously known, and the titanium being estimated volumetrically, the difference gives the quantity of zirconia. The permanganate should be previously standardised by means of iron by Margueritte's process.

If fluotitanate of potassium, or titanic acid in hydrochloric acid to which an alkaline fluoride has been added, is reduced by zinc, the liquid is no longer violet, but greenish, probably because a sesquifluoride of titanium is then formed instead of a sesquichloride. The results of the estimation by permanganate are, however, the same in each case.

Zirconia may be detected in titanic acid by taking advantage of its reaction on turmeric paper. A solution of zirconia in hydrochloric acid colours

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CHAPTER IV.

CHROMIUM, URANIUM, VANADIUM, TUNGSTEN.

CHROMIUM.

Estimation of Chromium.

PROFESSOR STORER has shown that chromic oxide is quickly changed to chromic acid when boiled with a mixture of concentrated nitric acid and chlorate of potassium. All the chromium in $\frac{1}{4}$ grm. of oxide of chromium, or of any of the ordinary chromium salts, can in this way be converted into chromic acid in a few moments; and even compounds as refractory as chrome-iron ore, or oxide of chromium which has been strongly ignited, can be oxidised in less time than would be required to complete their oxidation by the process of fusion ordinarily employed.

Mr. A. H. Pearson, experimenting on this process, finds that the chromic acid thus formed in the wet way can be readily and accurately estimated in the form of chromate of barium, if care be taken to wash the precipitated chromate with acetate of ammonium, or some other saline solution in which chromate of barium is insoluble. Anhydrous chromic oxide is placed in an evaporating-dish, together with a quantity of nitric acid and some chlorate of potassium, and covered with an inverted funnel with a bent stem. The acid is heated, and fragments of chlorate of potassium are added to it from time to time, until the chromic oxide has completely disappeared. This result is attained in the course of half an hour. The acid solution is diluted with water, then neutralised with ammonia, and the ammoniacal solution in its turn treated with enough acetic acid to make it slightly acid. After the acidulated solution has become cold, a solution of chloride of barium is added to it in slight excess, and the mixture is left at rest for ten or twelve hours. The precipitated chromate of barium is washed by decantation with a cold solution of acetate of ammonium, then collected on a filter, rinsed with water, dried, heated in a crucible to expel the last traces of water and of the ammonium-salt, and weighed.

The precipitate of chromate of barium must be allowed to stand for some time before filtering, lest it pass through the pores of the filter, and render the filtrate cloudy. The acetate of ammonium employed for washing

serves to dissolve any nitrate of barium or chloride of barium which may have been precipitated with the chromate; it has the further advantage of dissolving less of the chromate of barium than pure water would.

Experiments on various compounds of chromium show that this process is tolerably exact. Estimations of chromium in different specimens of sesquioxide gave 68·31, 68·65, 68·60, 68·31 per cent. Theory requires 68·62 per cent.

Chromic acid may also be estimated by adding nitrate of protoxide of mercury to its quite cold solution, neutralised with carbonate of sodium or with nitric acid; the orange-red precipitate of chromate of mercury should be allowed to stand for some hours before filtering, and after being washed with a weak solution of nitrate of mercury, and dried, is heated to redness in a platinum crucible, when it leaves pure green sesquioxide of chromium.

Volumetric Estimation of Chromic Acid.

Add to the chromic acid solution a sufficient quantity of iodide of potassium, free from iodate, and pure hydrochloric acid. This mixture is left quietly standing for from half an hour to a few hours' time, according to the degree of concentration of the solution, for in no case is the reduction of the chromic acid by means of the hydriodic acid instantaneous. When the reduction is complete, which may be learned from the pure green colour the liquid has assumed, a small quantity of thin starch paste is added, and the quantity of iodine which has been set at liberty is estimated by titration with a solution of hyposulphite of sodium. This plan, first proposed by C. Zulkowsky, gives sufficiently accurate results, and in some cases may be found useful; but it requires care, and is inferior to gravimetrical estimation.

For the valuation of chrome iron ores see Iron.

URANIUM.

Estimation of Uranium.

H. Rose* recommends the employment of sulphide of ammonium as a precipitant for uranium, as it completely separates this metal from its solutions, provided they are previously saturated with ammonia. No inconvenience attends the presence of a quantity of ammoniacal salts in the solution, excepting, of course, carbonate of ammonium and alkaline carbonates in general. The precipitate is black, but with a large excess of sulphide it may be reddish-brown. It is to be washed with water containing a little sulphide of ammonium. The precipitate contains no sulphide of uranium, but consists essentially of protoxide of uranium.

After desiccation it is roasted, to expel any sulphur which may adhere to

* Pogg. Ann., cxvi., 352.

it; it is then calcined at a high temperature in a current of hydrogen, and left to cool.

Pure protoxide of uranium is thus obtained. Should the solution contain much salts of potassium, or other strong non-volatile base, the precipitate may retain a little of them.

If a rapid process is required for the estimation of the commercial value of uranium, the following process of Patera's will give sufficiently accurate results, although it is not so reliable as the one just described.

A weighed quantity of the mineral is dissolved in nitric acid, taking care not to employ a large excess of acid. The solution is diluted with water, and, without filtering, supersaturated with carbonate of sodium. It is now boiled to complete the solution of the uranium, and to promote the separation of the carbonates of iron, lime, &c. The filtered solution of oxide of uranium in carbonate of sodium now contains only traces of foreign substances, and the uranium will be precipitated in the form of uranate of sodium with an excess of acid, on the addition of caustic soda. The orange-yellow precipitate is collected on a filter, washed for a short time, and then dried. It is then removed from the filter and heated to redness in a platinum crucible, the ashes of the filter, burnt apart, being added to the precipitate. The mixed residues are now placed on another filter and again washed, dried, and ignited, as before. The residuum of this second calcination is acid uranate of sodium, from the weight of which the amount of uranoso-uranic oxide in the mineral may be calculated. 100 parts of the uranate of sodium represent 83 parts of uranoso-uranic oxide.

Volumetric Estimation of Uranium.

The author prefers Guyard's process for this estimation, which depends on the precipitation of an insoluble triple phosphate of ammonium, uranium, and manganese, when an acid solution of phosphate of manganese is added to an acid solution of acetate of sesquioxide of uranium and ammonium.

The test solution of phosphate of manganese is prepared as follows:—Phosphoric acid solution of a syrupy consistency is heated in a platinum dish, and sesquioxide of manganese in fine powder is added by degrees, stirring frequently. The mixture is then heated for some time, and when the fused mass assumes a blue tint, and the phosphoric acid begins to volatilise, it is allowed to cool. It then becomes purple, and if dissolved in water it forms a purple solution resembling that of a permanganate. This solution is diluted, so that 30 c.c. shall represent one gramme of metal. The tinctorial power of phosphate of manganese is very weak.

To titrate this solution use a known quantity of pure sesquioxide of uranium in the form of acetate. The precipitate appears white with a yellowish shade. As soon as the precipitation is complete the precipitate

has a rose colour. It must be remembered that the presence of oxalate of ammonium interferes with the reaction.

To apply this process to ores, &c., dissolve a gramme or more of the substance in nitric or hydrochloric acid, or a mixture of the two. The solution is then supersaturated with carbonate of ammonium, which separates sesquioxide of uranium from the metallic oxides which so often accompany it. In many cases this operation suffices; but if the ore contains phosphorus or arsenic, or an oxide soluble in carbonate of ammonium, the uranium must be precipitated by ammonia and sulphide of ammonium in the state of protoxide, as already described, and filtered off. The precipitate is dissolved in carbonate of ammonium, and then transformed into the acetate of the sesquioxide. In any case the uranium must be brought into this state before estimation; but oxalic acid must be absent.

The solution is now diluted with about a litre of cold water, and then the standard solution of phosphate of manganese is gradually added from a burette until the whitish precipitate of phosphate of uranium, manganese, and ammonium appears rose coloured. This process is very rapid, and with a little practice is accurate.

In testing for uranium with ferrocyanide of potassium, it must be borne in mind that the presence of oxalate of ammonium prevents the formation of the red precipitate.

Separation of Uranium from most Heavy Metals.

Uranium may be easily separated by H. Rose's method from metals which are precipitated from their solutions by sulphide of ammonium, in the following manner:—Add to the solution an excess of carbonate of ammonium mixed with sulphide. All the oxides which the sulphide transforms into sulphides are precipitated, while the protoxide of uranium is dissolved in the carbonate of ammonium. Leave it to deposit in a closed vessel, wash the precipitate by decantation in water containing carbonate and sulphide of ammonium, and filter. Gently heat the filtered liquid to expel most of the carbonate, decompose the sulphide by hydrochloric acid, oxidise the protoxide of uranium with nitric acid, and precipitate the oxide of uranium by ammonia. If the operation is quantitative it should, before weighing, be calcined in a current of hydrogen.

Separation of Uranium from the Cerium Metals.

Wolcott Gibbs's method of precipitating the cerium metals with sulphate of sodium in the form of double sulphates of sodium with cerium, lanthanum, and didymium will effect this separation perfectly. These double sulphates are perfectly insoluble in a saturated solution of sulphate of sodium, whilst the double sulphate of sodium and sesquioxide of uranium is readily soluble,

and may be easily washed out from the highly crystalline insoluble double sulphates of the cerium group.

Separation of Uranium from Phosphoric Acid.

In laboratories where the estimation of phosphoric acid by the uranium process is frequently practised, it occasionally becomes advisable to effect the separation of uranium from the acid. M. Reichardt describes the following plan, which has proved very successful in the author's laboratory:—Dissolve the phosphate of uranium in hydrochloric or nitric acids, apply heat, add excess of perchloride of iron, and next, excess of solution of carbonate of sodium, wherein, aided especially by the large quantity of carbonic acid which is thus set free, the oxide of uranium is readily dissolved, while the phosphoric acid is combined in an insoluble form with the oxide of iron. The solution of oxide of uranium in carbonate of sodium is acidified with hydrochloric acid, boiled to expel carbonic acid, and the oxide of uranium finally precipitated with ammonia.

VANADIUM.

Preparation of Vanadic Acid from Vanadate of Lead.

The simplest method is the following, for which the author is indebted to Professor Wöhler:—Finely pulverise the mineral and attack it with a mixture of concentrated hydrochloric acid and alcohol; wash the precipitated chloride of lead with alcohol, and drive off the hydrochloric acid by means of heat from the blue solution of chloride of vanadium. This solution, treated by excess of caustic soda, deposits oxide of vanadium, which may be converted into vanadic acid by a current of chlorine.

For the following method of preparing vanadic acid on the large scale from the cobalt bed sandstone at Mottram, the author is indebted to his friend Dr. Roscoe, whose researches on the chemistry of this metal (Phil. Trans., 1868, p. 1, and 1869, p. 679) have afforded so great an insight into the properties of this remarkable element.

The sandstone possesses a light colour, and contains from 0·1 to 0·3 per cent of the oxides of cobalt, nickel, and copper. These metals are extracted commercially by the Alderley Edge Copper Mining Company; the ore is crushed and digested with hydrochloric acid; bleaching liquor and milk of lime are then added to alkaline reaction; a portion of the copper, together with the whole of the nickel and cobalt, remains in solution, whilst the small portion of vanadium which the ore contains falls down in the precipitate. It was from this precipitate that Dr. Roscoe was fortunate enough to secure a plentiful supply of this rare metal. A rough analysis of the crude lime precipitate showed that it contained about 2 per cent of vanadium, together with lead, arsenic, iron, lime, and sulphuric and phosphoric acids.

In order to prepare pure vanadium compounds in quantity from this material, 3 cwts. were dried and then finely ground with four times its weight of coal, and the mixture well furnaced with closed doors for several days until the greatest part of the arsenic had been driven off. The coal having been thus burnt off, the mass was then ground up with one quarter of its weight of soda-ash, and well roasted in a reverberatory furnace with open doors for two days to oxidise the vanadium to a soluble vanadate; the mass was then lixiviated, and the solution drawn off from insoluble matters; the liquid was acidified with hydrochloric acid, and sulphurous acid was then passed into the solution to reduce the arseniates, when the remaining arsenic was precipitated by sulphuretted hydrogen. The deep blue solution thus obtained was carefully neutralised by ammonia (an excess causes much of the vanadium to pass into solution), the precipitated oxide of vanadium washed on cloth filters, oxidised by nitric acid, and evaporated to dryness. The well-dried crude vanadic acid was then boiled out with a saturated solution of carbonate of ammonium, which left oxide of iron, sulphate of calcium, alumina, &c., insoluble, and the filtrate evaporated until the insoluble vanadate of ammonium separated out. This crude vanadate was then washed with sal-ammoniac solution to free it from sodium salts, and re-crystallised.

In order to prepare pure vanadic acid from this salt, it was roasted in the air, and the powdery acid obtained was suspended in water into which ammonia gas was passed; the dissolved vanadate of ammonium was separated by filtration from a residue containing silica, phosphates, &c., and was crystallised by evaporation in platinum.

Another method of preparing pure vanadic acid is to obtain the pure oxychloride, and decompose this by water, when vanadic acid is yielded as a fine orange-coloured powder. The oxychloride is prepared by intimately mixing sugar charcoal with crude vanadic acid, and heating the mixture to redness in a current of hydrogen. After cooling in hydrogen, the mixture of trioxide and carbon is removed to a hard glass retort heated by a large Bunsen's lamp, and a current of dry chlorine gas passed in. The crude oxychloride comes off as a reddish-yellow liquid, which is purified by distillation in a current of carbonic acid, and afterwards rectified several times over clean sodium. It is a yellow-lemon liquid, boiling at 126·7° C.

Purification of Vanadic Acid from Phosphorus.

Dr. Roscoe has found that phosphorus is very difficult to separate from vanadium. The action of even traces of phosphoric acid on vanadic acid is most remarkable; if present in quantities exceeding one per cent of the weight of the vanadium, it altogether prevents the crystallisation of the vanadic acid, and the fused mass possesses a glassy fracture and a black

vitreous lustre. If much phosphorus is contained with the vanadium, the method which has proved most effectual for its removal is to deflagrate the finely divided impure acid with its own weight of sodium in a well covered wrought-iron crucible, and wash the resulting mixture of vanadium oxides by decantation until the wash-water ceases to give an alkaline reaction; frequently this operation has to be repeated three times before the molybdenum test ceases to indicate phosphorus.

TUNGSTEN.

Preparation of Tungstic Acid from Wolfram.

The following process, due to Professor Wöhler, has been found to answer very well. Reduce the wolfram (a tungstate of iron and manganese) to fine powder, and digest at a gentle heat in a mixture of four parts strong hydrochloric and one part nitric acid, till yellow pulverulent tungstic acid is left behind. Wash this by decantation, dissolve in ammonia, and evaporate the solution to the crystallising point. The resulting tungstate of ammonium calcined in the air leaves pure yellow tungstic acid.

When the impure tungstic acid is dissolved in ammonia, a residue will be left which contains, besides undecomposed wolfram, small white grains composed of silica and columbic acid, and constituting about two per cent of the wolfram.

CHAPTER V.

ZINC, ALUMINIUM, IRON.

ZINC.

Precipitation of Metallic Zinc.

WHEN metallic magnesium, as met with in commerce, is introduced into a slightly acidulated solution of sulphate of zinc (or other zinc salt) hydrogen is evolved, and a precipitation of a spongy bulky mass of metallic zinc occurs. If this sponge is washed till free from soluble salts, then dried and pressed in a steel-crushing mortar between the jaws of a powerful vice, a brilliant solid lump of zinc is produced.

Volumetric Estimation of Zinc.

When a solution of a zinc salt is added to a known quantity of solution of ferrocyanide of potassium, there is formed a precipitate of ferrocyanide of zinc, insoluble in ammonia. By estimating the amount of ferrocyanide of potassium remaining in solution by means of permanganate of potassium, the amount of zinc present can be readily calculated. Upon this reaction M. Renard has based the following process:—Dissolve a known weight (one or two grammes) of the substance to be assayed for zinc in aqua regia, add excess of ammonia, filter from the precipitate and wash well. To the filtrate 25 c.c. of a solution of ferrocyanide of potassium (150 grammes to the litre) are added; the solution is made up to 250 c.c., and filtered; 100 c.c. of the filtrate are measured into a glass vessel, and neutralised with pure hydrochloric acid free from chlorine and sulphurous acid. Afterwards the solution is rendered strongly acid with about 30 c.c. of the same acid and titrated permanganate solution added until the whole of the yellow prussiate is transformed into red prussiate. By calculation the amount of zinc contained in the substance is arrived at. None of the metals commonly present in minerals, such as iron, aluminium, manganese, lead, &c., influence the process. Either they are precipitated by the ammonia, or they are not precipitated by ferrocyanide of potassium. Copper is an exception, and, if present, interferes with the process.

Precipitation of Zinc as Ferrocyanide.

A good method for volumetrically determining the amount of zinc in ores is given in the "Zeitschrift für Analytische Chemie," for 1869, by Maurizio Galetti, Chief Assayer at the Royal Assay Office, Genoa. The following is a description of the process:—Supposing sulphide of zinc (blende) is to be assayed, about half a gramme of the finely pulverised ore is to be treated with concentrated nitric acid, and boiled to incipient dryness, until the sulphur left undissolved does not contain any particles of undissolved ore. Then add strong hydrochloric acid, and boil again until no nitric acid is left. Calamine (carbonate of zinc) should at once be acted upon with hydrochloric acid: but, in order to make sure of the complete oxidation of all the iron the ore may happen to contain, it is best to add to the acid a few decigrammes of pure chlorate of potassium. After having boiled this solution for a few minutes, it is diluted with distilled water; a large excess of ammonia is added to the solution, which is then boiled and slightly acidified with acetic acid. After brisk agitation, boil again for a few minutes, and then supersaturate with ammonia. The liquid is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the fluid up to half a litre. This having been done, the fluid is very cautiously and gradually acidified with dilute acetic acid, one part acid sp. gr. 1·07 to 10 of distilled water. Any large excess of this should be avoided, as the solution should only be very slightly acid. As soon as the basic acetate of iron has subsided, the precipitation of the zinc by means of a standard solution of ferrocyanide of potassium may be proceeded with.

The ferrocyanide solution is made by dissolving 41·25 grms. of the said salt in as much distilled water as will make the solution weigh exactly one kilogramme.

The presence of compounds of lead (as, for instance, carbonate, sulphate, or sulphide of lead) occurring along with the ores of zinc, does not interfere with the completeness of the precipitation of zinc as ferrocyanide of zinc. This even holds good up to 10 per cent of metallic lead. Since some ores of zinc, especially calamine, often contain manganese, it is best to add to the ammoniacal solution, before any acetic acid is added, a few drops (from 2 to 4) of bromine, in order to convert the protoxide of manganese into proto-sesquioxide, leaving the solution standing for twenty-four hours after the addition of the bromine.

The ammoniacal solution of chloride of zinc being colourless, there should be added to it, previous to cautious acidification by means of dilute acetic acid, a few drops of tincture of litmus, in order to more readily hit the precise point of sufficient acidification, which is known by the blue colouration changing to a rose-red.

The ferrocyanide of zinc which is mixed with oxide of iron preserves its naturally white colour as long as the liquid contains free zinc, but its colour changes to a greyish-white as soon as a very slight excess of the ferrocyanide standard solution is present; the liquid also then becomes turbid, and the precipitate settles very slowly. By these characteristic signs, the end of the operation may be always recognised. In order to make sure, the liquid should be touched with a glass rod which has been just previously moistened with a dilute solution of ammoniacal nitrate of copper; this will have the effect of indicating any excess of the ferrocyanide solution, by producing the more or less intense colour characteristic of ferrocyanide of copper. The zinc solution should be at a temperature of from 40° to 50°, whereby the rapid subsidence of the ferrocyanide of zinc is promoted.

Filtration is not necessary, as the presence of the gelatinous silica (due to the decomposition of silicates of zinc occurring in the ores of that metal) does not interfere with the correctness of this method of estimating zinc quantitatively.

Precipitation of Zinc as Oxalate.

A very ingenious method of estimating zinc as well as other metals, and one which, in the author's hands, has proved very accurate, has recently been worked out by Mr. W. Gould Leison, of the Lawrence Scientific School ("Silliman's Journal," Sept., 1870). The process is as follows:—The zinc compound is obtained in the form of a sulphate, and to a neutral solution of this salt oxalic acid and then a large quantity of strong alcohol are added. Oxalate of zinc precipitates in the form of an extremely fine powder. This is filtered through sand, thus:—A slight funnel is ground conical near the throat. A little pear-shaped piece of glass with a long stem is then dropped into the funnel, stem upwards, so as to form a valve, impassable to sand laid upon the ball of the glass, but allowing liquids to pass freely. By means of the stem the valve can be lifted from its seat, and the sand and oxalate of zinc, after washing with alcohol and careful drying, are washed together into a flask with hot dilute sulphuric acid. A few c.c. of strong sulphuric acid are then added, and the solution titrated with permanganate of potassium. From the amount of oxalic acid thus found the quantity of zinc can readily be calculated.

Precipitation of Zinc as Sulphide.

All who have experienced the difficulty of filtering and thoroughly washing the light, slimy precipitate of sulphide of zinc, as ordinarily obtained, will be glad to know of a modification of the usual mode of precipitation (due to Mr. J. H. Talbot, of the Lawrence Scientific School), whereby this difficulty is avoided. The solution of zinc, if acid, is to be

neutralised as nearly as possible by carbonate of sodium or ammonium. To the boiling solution sulphide of sodium or ammonium is to be added, a large excess being very carefully avoided. The white precipitate, on continued boiling, soon becomes granular, and settles readily. The supernatant clear liquid is then to be tested with a drop of the alkaline sulphide, to be sure of complete precipitation, and the sulphide then washed with hot water. The filtrate is perfectly clear and quite free from zinc; the washing is easy and rapid. The sulphide of zinc is next to be partially dried with the filter, brought into a porcelain crucible, and ignited, at first gently and afterwards strongly, with free access of air. The expulsion of the last traces of sulphuric acid is much facilitated by occasionally dropping fragments of carbonate of ammonium into the crucible. Pure oxide of zinc finally remains, the ignition being continued until a constant weight is obtained. The results in this way are very accurate.

Separation of Zinc from Uranium.

To a nearly neutral and somewhat dilute solution of the two metals add acetate of sodium in excess, boil, and pass sulphuretted hydrogen through the boiling solution till all the zinc is precipitated as sulphide. Filter quickly, wash, and finish as described in the last paragraph.

Separation of Zinc from Chromium.

Obtain the zinc and sesquioxide of chromium in the form of nearly neutral solution, by the addition, if necessary, of carbonate of sodium, then add excess of acetate of sodium, and oxidise the chromium to the state of chromic acid by a current of chlorine, or (if it be present in small quantity only) by addition of chlorine water, or bromine. The solution should be kept hot and as neutral as possible by the cautious addition of carbonate of sodium. When the oxidation is complete expel the excess of chlorine or bromine by heat, and add acetate of barium, which will precipitate the whole of the chromium present in the form of chromate of barium, taking the precautions already described at p. 54.

The oxidation of the chromium to the state of chromic acid may also be effected by Professor Storer's method, with nitric acid and chlorate of potassium, as described at p. 54.

Separate the excess of barium from the solution by addition of sulphuric acid, and then precipitate the zinc with carbonate of sodium; or the acid solution may be supersaturated with ammonia so as to re-dissolve the oxide of zinc, filtered, if necessary, to remove iron, &c., and the zinc precipitated by sulphuretted hydrogen. When sulphate and chromate of barium are thrown down together, the chromic acid may be reduced to sesquioxide by boiling with concentrated hydrochloric acid and alcohol, after which the

barium may be precipitated by sulphuric acid, and the sesquioxide of chromium thrown down in the filtrate by boiling with ammonia in the usual manner. As the reduction of chromate of barium by means of hydrochloric acid and alcohol does not take place very readily, it is better to boil the chromate with an excess of carbonate of potassium or sodium, to filter off the carbonate of barium, and determine the chromic acid by means of nitrate of protoxide of mercury, as explained at page 55, or by reduction to oxide of chromium and precipitation with ammonia in the usual manner.

ALUMINIUM.

Precipitation of Alumina.

Sulphide of ammonium is a more complete precipitant for alumina than caustic ammonia or carbonate of ammonium, and should always be employed in preference when practicable. The small quantity of free sulphur which will be generally precipitated at the same time is driven off on ignition. It must be remembered that oxalic acid and its salts possess in a slight degree the property of most non-volatile organic acids, of impeding certain reactions of alumina; therefore, when oxalate of ammonium is present in great excess, alumina is not immediately precipitated by ammonia and sulphide of ammonium; although, in the course of a little time, according to its proportion, alumina is precipitated, especially if the solution be heated.

Separation of Aluminium from Zinc.

The metals should preferably be in the form of chlorides. Dilute the solution considerably, render it neutral or nearly so, add acetate of sodium in excess, and then boil for a short time, adding a drop of free acetic acid occasionally; the whole of the aluminium will be precipitated in the form of basic acetate. Filter rapidly through a ribbed filter, and keep the liquid as near the boiling point as possible during filtration. If an absolutely complete separation is necessary, re-dissolve the precipitate in dilute hydrochloric acid and repeat the operation. From the solution the zinc is completely precipitated by sulphuretted hydrogen.

Separation of Aluminium from Uranium.

The separation of these two metals may be effected in the same manner as that of aluminium and zinc above described.

Separation of Aluminium from Chromium.

To a strong solution containing these two metals add chlorate of potassium and concentrated nitric acid; the chromium is quickly oxidised to chromic acid. Or the same thing may be effected by means of chlorine or

bromine, as described at p. 63. The chromic acid is then precipitated with chloride of barium, taking the precautions described at p. 54. With care, this process gives very accurate results.

Another, and under some circumstances, a better plan, is the following, for which the author is indebted to Professor Wöhler. Pass chlorine through the solution of the sesquioxides of chromium and aluminium in caustic potash, until all the chromium is oxidised to chromate. The aluminium will then be in the form of precipitated hydrate, with the exception of a small quantity, which is readily precipitated by digestion with carbonate of ammonium. Filter the solution of chromate of potassium from the alumina, and to the filtrate add alcohol and excess of hydrochloric acid, and heat till the reduction to sesquioxide of chromium is complete. Add ammonia to the warm solution, when the whole of the chromium will be precipitated as sesquioxide.

Separation of Aluminium from Glucinum.

These metals may be separated by precipitating the aluminium in the form of basic acetate, as described at p. 65 (Separation of Aluminium from Zinc). The glucina may be precipitated in the filtrate by ammonia.

Wolcott Gibbs adds a solution of fluoride of sodium to the one of aluminium and glucinum, when the whole of the aluminium is thrown down in the form of cryolite, while the glucinum remains in solution. From this solution ammonia precipitates the glucina.

When hyposulphite of sodium is added to a nearly neutral dilute solution containing aluminium and glucinum, and the liquid is boiled until no more sulphurous acid is disengaged, the aluminium is precipitated (together with some sulphur), whilst the glucinum remains in the solution.

Separation of Aluminium from the Cerium Metals.

Bring the metals to the form of sulphates dissolved in a small quantity of water, and add sufficient powdered sulphate of sodium to form a saturated solution. The cerium metals immediately separate in the form of double sulphates with sulphate of sodium, as a white highly crystalline powder. Filter off and wash with a saturated solution of sulphate of sodium. Precipitate the aluminium from the filtrate by addition of ammonia and sulphide of ammonium, and dissolve the double sulphates of sodium and cerium, &c., in dilute hydrochloric acid, and precipitate with oxalate of ammonium.

Separation of Aluminium from Magnesium.

These, when in solution together, may be separated by Dr. Gibbs's plan, viz., boiling the dilute solutions with excess of acetate of sodium, and a

little acetic acid, whereby all the aluminium is precipitated as basic acetate. The details of the operation are conducted as in the Separation of Aluminium from Zinc (p. 65).

Insoluble mixtures containing aluminium and magnesium, such as spinel (aluminate of magnesium), are best analysed by the process given by Wöhler. Fuse the finely levigated mineral with six times its weight of bisulphate of potassium, and keep the mass fused at a red heat till sulphuric acid is no longer disengaged. Dissolve the fused mass in water acidified with hydrochloric acid, and decompose it with sal-ammoniac, which precipitates the alumina. To prevent any magnesia coming down with the alumina, care must be taken to keep the liquid boiling till no more free ammonia is given off. The gelatinous alumina, which the boiling liquid deposits, is filtered, but as it is almost impossible to wash in this state, it must be allowed to half dry on the filter, when it can be washed perfectly. The magnesium is precipitated from the filtrate by ammonia and phosphate of sodium.

Separation of Aluminium from Calcium.

The method of separating calcium from aluminium by means of ammonia has been improved by H. Rose. Instead of being careful to employ ammonia free from carbonic acid, and avoiding the presence of this gas, he heats to gentle ebullition the liquid in which the alumina has been precipitated by excess of ammonia. When the evolution of ammonia ceases, all the aluminium is in the precipitate, and may be separated by filtration without requiring any special precaution, for the simple reason that in the presence of ammoniacal salts the carbonate of calcium is decomposed, the calcium entering into solution. A little sal-ammoniac may even be added, if there is a chance of there not being sufficient to favour this decomposition.

When the calcium is present in small quantities only, tartaric acid may be added, and the solution then supersaturated with ammonia. The calcium is precipitated in the form of tartrate if there is only a little aluminium present; otherwise, much remains in solution. In either case, however, oxalate of ammonium will separate it perfectly in the form of oxalate of calcium.

IRON.

Preparation of Pure Iron.

The preparation of metallic iron in an absolutely pure state is a problem of enormous difficulty; in fact, it is only recently that it has been effected in a satisfactory manner. The British Association for some years past have had a committee, consisting of F. A. Abel, D. Forbes, and A. Matthiessen, investigating the subject, and their reports have been presented from year to year to the chemical section of the association. The plan finally

adopted by the committee is as follows :—Pure dried protosulphate of iron and pure dried sulphate of sodium are mixed in nearly equal proportions, and introduced gradually into a red-hot platinum crucible. The mass is kept in fusion until the evolution of sulphurous acid gas ceases. The crucible is then allowed to cool, and the fused mass is extracted with water. If the heat be properly regulated, the whole of the iron is left as a very fine crystalline oxide. This oxide is thoroughly washed by decantation to remove every trace of the sulphate of sodium, and after being dried, is reduced by hydrogen in a platinum crucible; the spongy iron thus obtained is pressed into solid buttons by means of a strong coining press and a diamond mortar, and then melted in lime crucibles, the lime having been previously burnt, slaked, and re-burnt, thus forming a fine impalpable powder, which is compressed in the crucible mould. The best method of fusion has been found to be as follows :—The lime crucible is placed in a slanting position on a piece of lime. A large oxyhydrogen blowpipe plays on the outside of the crucible, whilst the flame of another is directed inside. When white-hot a cylinder of the compressed iron is thrown into it. It quickly melts, but at the expense of a large quantity of the iron which is oxidised, the amount so lost varying between 25 and 50 per cent. In order to obtain a good solid button of melted iron, it is necessary to cool it in an atmosphere of hydrogen, which is easily obtained simply by turning off the oxygen from the blowpipe playing inside the crucible. On analysis it was found that buttons so prepared, weighing about 15 grammes each, were free from phosphorus, silicon, and calcium, and only contained sulphur to the extent of from 0·00025 to 0·0007 per cent.

Metallic magnesium put into a solution of a proto- or sesqui-salt of iron, causes an evolution of hydrogen, and a precipitation of metallic iron in the pulverulent state. When freed from the saline solution by washing, then dried and compressed, this metallic sponge possesses great brilliancy, and dissolves in acids without leaving any residue, and without communicating any odour to the hydrogen. As the distilled magnesium of commerce is almost chemically pure, and as salts of iron can readily be freed from impurities by crystallisation or other means, this affords a good method for obtaining pure iron. The compressed metallic sponge is consolidated, as above described, by heating in lime crucibles before the oxy-hydrogen blowpipe.

Estimation of Protoxide of Iron in the Presence of Peroxide.

Messrs. Wilbur and Whittlesey have carried out a suggestion of Avery,* and applied it very successfully to the estimation of ferrous and ferric oxides in silicates. Avery found that silica and many silicates can be

* Chemical News, vol. xix., p. 270.

readily and completely dissolved by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

These chemists have applied this observation to the estimation of the two oxides of iron, and have obtained such satisfactory results that their process deserves to be generally adopted for the estimation of iron in silicates. The method is as follows:—A quantity of the finely-powdered silicate to be examined is weighed in a platinum crucible; as much, or rather more than as much, powdered fluor spar (or of powdered cryolite), free from iron, is poured into the crucible; the powders are thoroughly mixed by stirring with a glass rod; the rod is wiped clean upon a fresh portion of the powdered fluoride; and the latter is thrown upon the mixture in the crucible. Strong hydrochloric acid is then poured into the crucible, until the powder is thoroughly drenched and the crucible about two-thirds filled with the liquid. The crucible is set upon a water-bath, and heated until the iron has all dissolved: the proportion of iron is finally determined by titrating with a standard solution of permanganate of potassium. To protect the mineral from the air during the process of solution, the crucible must be kept full of some non-oxidising gas, which can be either carbonic acid or coal gas, as may happen to suit the convenience of the operator.

If carbonic acid be used, it is sufficient to cover the crucible with a bit of sheet-lead, perforated with two holes, through one of which is thrust a glass tube communicating with a gas-bottle in which the carbonic acid is generated, while the other serves as an outlet for the escape of carbonic acid and acid vapours. The crucible is, in this case, simply set upon an ordinary water-bath.

When coal-gas is used (and this agent is to be preferred on the whole), the apparatus may be arranged as follows:—Set the charged platinum crucible upon a glass or leaden tripod, inside a wide beaker, in the bottom of which there is about an inch of water. Invert a narrower beaker within the first, so that its mouth shall be sealed by the water and the crucible be enclosed in a transparent chamber. Coal-gas is led into this chamber through a bent glass tube, which passes down between the side of the upright and that of the inverted beaker, and delivers the gas near the top of the chamber. The surplus gas escapes through another tube similarly bent, which starts from a point below the crucible, and is burned in the outer air. To facilitate the passage of the glass tubes, the mouth of the inverted beaker may be made to rest upon three or four bits of stone or metal, or an orifice large enough to admit the tubes may be made upon the rim of the beaker. During the process of solution, the upright beaker is kept immersed in water, at or near the temperature of boiling. In case the coal-gas should contain any sulphuretted hydrogen, it would be well to purify it by means of a potash-tube. An hour and a half is ample for the solution of the iron

in 0·5—1 grm. of finely-powdered trap rock. Fifteen minutes, on the other hand, will suffice for the solution of 0·2 grm. of iron wire. Instead of hydrochloric acid, sulphuric acid may be used to act upon the mixture of fluor spar and mineral. The sulphate of calcium frequently formed is objectionable, from its liability to envelope portions of the mineral, and to protect the iron from being dissolved, rather than from any tendency to interfere with the actual titration.

Experiments have shown that the presence of sesquioxide of iron does not interfere in any way with the estimation of the protoxide. Commercial iron-alum, which of itself has no decolourising action on permanganate of potassium has none after it has been heated with cryolite and hydrochloric acid. It is found, also, by acting upon weighed quantities of iron wire mixed with cryolite and iron-alum, that the iron can be estimated as well in the presence of the alum as in its absence, provided only that the metallic iron be dissolved in hydrochloric acid, with the necessary precautions to prevent oxidation, before adding the other ingredients of the mixture. If the iron wire, cryolite, and ferric alum were treated all at once with acid, some of the hydrogen generated by the solution of the metallic iron would reduce a part of the ferric salt; so that, in the final titration, more iron would be found than was introduced into the mixture in the form of wire.

If time enough be allowed, finely-powdered sesquioxide of iron can be dissolved in this way, even after intense ignition.

To estimate sesquioxide of iron in a silicate, a separate portion of the mineral may be treated with fluor spar and acid, the solution reduced by zinc in a small flask in the usual way, and the total amount of iron determined with chameleon. Or, if the mineral contains only a small proportion of ferric oxide, it will be sufficient to put a bit of zinc into the crucible with the mixture of mineral, fluor spar, and acid. The difference between the total iron and that determined as protoxide is calculated as peroxide.

A. H. Allen has pointed out that a little irregularity in the results of the above process arises from the employment of hydrochloric acid as a solvent. It has been repeatedly shown that the presence of hydrochloric acid interferes appreciably with the estimation of iron by permanganate, while it does not affect Penny's bichromate process. If the former oxidising agent be employed, the solution should be effected by means of sulphuric acid.

Mr. Allen effects solution of difficultly soluble ores by heating with hydrochloric acid under pressure. This method has been used very successfully in the analysis of various titanic iron ores and sands. About a gramme of the finely-powdered mineral is heated in a sealed piece of combustion tubing, half full of fuming hydrochloric acid. At first the heat of a water-

bath is sufficient, but after a few hours the temperature is gradually raised to 140° or 150° C. The ore is completely decomposed in four or five hours, and after the tube has cooled the end may be broken under water, and the ferrous oxide at once estimated by bichromate. The same method will yield a solution suitable for the determination of the other constituents of the ore.

Reduction of Sesqui-Salts of Iron to Proto-Salts.

Sulphurous acid or metallic zinc is the reducing agent usually employed, but a much more effectual and rapid agent has been proposed, in sulphuretted hydrogen, by Mr. Reynolds. This answers much better than either zinc or sulphurous acid. The reduction, even in a strongly acid solution, takes place immediately; and on boiling until the sulphuretted hydrogen is expelled, the sulphur separated coagulates completely; so that, after allowing the solution to cool in the flask in which it has been boiled, a cork being placed in the neck during the cooling, filtration may be effected so rapidly that no oxidation need be feared, and the determination may then be effected with permanganate, as usual. It is better to add a considerable quantity of water to the solution before reduction, to avoid the oxidation which would afterwards ensue in the filtration of a concentrated solution of protoxide of iron.

Volumetric Estimation of Iron by Hyposulphite of Sodium.

M. Mohr has shown that the direct estimation of perchloride of iron, by means of a solution of hyposulphite of sodium, does not give satisfactory results. The cause of error lies chiefly in the decomposing action exercised by free hydrochloric on hyposulphurous acid.

By using sufficiently diluted acetic instead of hydrochloric acid, or by treating the weak hydrochloric solution by acetate of sodium, it will be found that the hyposulphurous acid is not decomposed, even after some length of time. Consequently, a solution of perchloride of iron may be estimated by means of a hyposulphite solution, taking care to add previously sufficient acetate of sodium to make apparent the red colour of the ferric acetate, and then sufficient weak hydrochloric acid to make this colour again disappear. Then pour into the solution a known quantity of hyposulphite, and estimate the excess of this reagent, which colours the liquid a deep violet, by means of starch paste and iodine solution.

Very exact results are obtained in this way; but care must be taken to use liquids not too much diluted; 0·00012 gramme is the minimum amount of iron which should be contained in 1 c.c.

One equivalent of perchloride of iron exactly decomposes two equivalents of hyposulphite of sodium.

Volumetric Estimation of Iron with Subchloride of Copper.

Subchloride of copper has been found by Dr. Winkler to be a very powerful reducing agent for sesquioxide of iron, analogous to protochloride of tin in its effects. But whilst protochloride of tin causes but a partial reduction in a cold solution, subchloride of copper acts directly with theoretical accuracy at the lowest temperature, and at any dilution. It is, therefore, particularly adapted for the volumetric determination of iron. The completion of the reduction may be ascertained with certainty by the addition of a few drops of sulphocyanide of potassium to the solution to be tested, when the well-known deep-red colour appears. When the subchloride solution is dropped into one of iron so coloured, the red colour becomes lighter and lighter, and finally disappears entirely. After the solution is bleached, the reduction of the iron is complete, and the next drop of copper solution causes a precipitation of subsulphocyanide of copper. This gives a double indication of the end of the reduction, namely, the bleaching of the red colour of the sulphocyanide of iron, and the cloudiness produced by the insoluble salt of copper. The rapidity and simplicity of the process, as well as the few accessories required, especially recommend this method to technical laboratories, where the want of a short and accurate process has long been felt.

The Solution of Subchloride of Copper is made by dissolving sheet-copper in nitric acid; evaporate, to drive off the excess of nitric acid; and dissolve the residue in water containing hydrochloric acid. This solution is put into a flask, and a quantity of common salt equal in weight to the residue of dry copper-salt is added, in order to prevent the separation of a precipitate of subchloride of copper during the subsequent reduction. Several pieces of sheet-copper are put in the flask, and the liquid is then heated to boiling. This is continued until the solution is nearly colourless, and all the chloride of copper has been changed to subchloride. The flask is then corked, and allowed to cool; the solution is then diluted with water containing hydrochloric acid, until 1 c.c. corresponds to 6 milligrammes of iron. In order to keep this solution without change for further use, it should be poured into a bottle, to which is fitted an air-tight stopper, and containing a spiral of thick copper wire reaching from the bottom to nearly the neck. This completely protects the subchloride of copper from oxidation, so that the strength of the solution remains nearly always the same. It is, however, best to determine the strength of the standard from time to time, since this requires but a few minutes. For this purpose, there is needed a—

Solution of Sesquichloride of Iron of known strength. This may be made, according to Fresenius, by dissolving in hydrochloric acid and chlorate of potassium 10·03 grms. of piano-wire, corresponding to 10·0 grms. of

pure iron, and diluting to 1 litre. For each test of the standard, 10 c.c. of this solution are taken, containing 100 milligrammes of iron.

In performing this volumetric determination of iron, there are but few rules to be observed. It is advisable that the solution to be treated be decidedly acid, and very dilute before it is brought under the burette. A solution that contains from 100 to 200 milligrammes of iron should be diluted to 500 c.c. or more.

In noting the end of the reduction, though it is not necessary that the solution of sulphocyanide of potassium should contain a known amount of this salt, yet it will be found better to use about the same strength at all times, since the presence of too much sulphocyanide makes the reaction less marked.

In adding the sulphocyanide, care must also be taken; for, if too much is added to the iron solution, although a deeper blood-red will be obtained, yet a difficultly-soluble subsulphocyanide of copper may separate, clouding the solution and re-dissolving with trouble. Four or five drops of solution are quite sufficient to be added. Then, by dropping in the copper solution, the bleaching takes place with extraordinary sharpness, and only when all the iron has become a protoxide does the next drop cause a permanent cloudiness.

The presence of coloured metallic compounds (such as salts of cobalt, nickel, and copper) does not in the least hinder the recognition of the reactions, if the solution is properly dilute. Neither does the presence of arsenic acid affect the process, since this is not reduced by subchloride of copper. This process, therefore, is important to the metallurgist, who is often compelled to determine quickly and correctly the amount of iron contained in a matt, or speiss, or other product. By the above process this is possible in an hour.

Volumetric Estimation of Iron with Permanganate of Potassium.

To ensure accuracy in this estimation, M. Moyaux has drawn up certain memoranda which deserve attention in order to secure uniformity of result. The titration of the permanganate solution can only be properly made by means of metallic iron, and, when the latter metal, in a sufficiently pure state for this purpose, is not at hand, oxalic acid should be employed. The use of ammonio-sulphate of iron for obtaining the standard should be rejected. Unless the precise composition of this salt is repeatedly ascertained, it is not to be relied on, and this testing is a loss of time. The evaporation of solutions of iron containing hydrochloric or other volatile acids, after the addition of sulphuric acid, always impairs the result of the titration. The reduction of solutions of per-salts of iron to proto-salts, after driving off excess of hydrochloric acid, is best effected by amalgamated

zinc if zinc is used at all, but this last metal is to be rejected when a solution of iron happens to contain, at the same time, a proto- and a per-salt. When 0·3 grm. of ore is taken for assay, in case the ore contains more than 40 per cent of metallic iron (or, when less than that quantity, 0·5 grm. is taken for assay), the quantity of fluid best suited to yield accurate results should not, in either of these cases, respectively exceed ¼ or ½ a litre.

Repetition in Volumetric Analysis.

When iron is determined by means of permanganate of potassium, all the iron is, at the end of the operation, in the form of sesquioxide, while there is also a very small excess of unreduced permanganate. Mr. Bryant Godwin proposes that, as a control, the solution should be boiled for a short time with pure zinc-dust, and rapidly filtered and washed with water (previously boiled to expel air). This reduces the iron again to ferrous oxide, and the process of titration may be repeated a second, and even many more, times, until the bulk of the liquid becomes too large to handle.

Estimation of Carbon in Iron and Steel.

This is a problem of considerable difficulty, and to secure accurate results many special precautions are necessary, owing to the large preponderance of the iron over the carbon present. The carbon may be present in two forms—as combined carbon, and as free or graphitic carbon. The estimation may be of the total carbon present, or of either the combined or graphitic separately, and the method of analysis adopted will have to be selected accordingly. The following is a description of the most satisfactory processes which have been devised for these estimations.

A. Estimation of the Total Carbon.—Bromeis, modifying Regnault's process, treats the iron as if it were an organic substance, and burns the carbon off:—About two inches of a combustion-tube of hard Bohemian glass, closed at one end, are filled with a mixture of equal parts of chromate of lead and chlorate of potassium. 3 grms. of the iron under examination, in a state of very fine division, are intimately incorporated with 50 grms. of a mixture of 40 parts of chromate of lead and 6 parts of previously fused chlorate of potassium, and introduced into the combustion-tube, and lastly a layer of chromate of lead. To the tube a chloride of calcium and a Liebig's potash apparatus are attached; the former to retain traces of moisture, the latter to absorb the carbonic acid formed. The combustion-tube is cautiously heated, first near the open end, as in the process of organic analysis. When the mixture of the iron with the lead salt is brought to a dull red heat, the metal burns with incandescence, and the carbon is oxidised to carbonic acid, which is absorbed by the potash

solution. At the close of the operation the mixture at the extreme end of the tube is heated, oxygen is evolved, all carbonic acid is driven forward, and the last traces of carbon consumed. From the increase of weight of the potash apparatus, due to carbonic acid, the amount of carbon may be calculated. Mr. Tosh, in reporting on this process, says that the results of different experiments agree well with one another. There is reason to think, however, that the percentage of carbon indicated is somewhat too low, on account of loss of carbon during pulverisation of the iron. This loss, as pointed out by Morfit and Booth,* is often appreciable, and in the case of highly graphitic iron, very considerable. With this one exception, the process is in every respect commendable, and where, as with spiegel-eisen or white iron, this loss of carbon cannot take place, it strongly recommends itself.

The process devised by Professor Wöhler is strongly recommended by Mr. Tosh, who has made many determinations by its means. It is carried out in the following way:—A weighed quantity of iron contained in a porcelain boat is placed in a hard glass tube, and exposed at a dull red heat to the action of chlorine (first dried by passing over pumice stone saturated with sulphuric acid) till no more perchloride of iron is formed. The whole of the carbon remains in the boat, which, when cool, is transferred into a porcelain tube, and the carbon burned in oxygen. An estimation by this method may be performed in two hours. Care must be taken to have the chlorine perfectly free from moisture, otherwise a portion of carbon may be lost by the formation of hydrocarbons. The results given by this process are very concordant. The perfect combustion of graphite, even in oxygen, requires a very high temperature. The most convenient plan is to place the graphite first in a platinum boat, insert this into a well glazed porcelain tube, and expose to a full red heat in a small charcoal furnace. In a gentle stream of oxygen the carbon is perfectly burned in a few minutes, and the resulting carbonic acid is absorbed in the usual way by potash solution.

Fresenius recommends that a weighed portion of the metal, in borings or chippings, be dissolved in dilute sulphuric acid by the aid of heat. The gases evolved during solution, consisting mostly of hydrogen, are passed over red-hot oxide of copper. The gaseous hydrocarbons are burned, and the carbonic acid formed, after drying by chloride of calcium, is absorbed by potash solution in a Liebig's apparatus, and thus weighed. This only gives the combined carbon, and when an estimation of the total carbon is required, the matter remaining behind, insoluble in the dilute sulphuric acid, is collected and burned in a stream of oxygen, and from the weight of

* Chemical Gazette, vol. xi.

the resulting carbonic acid the amount of carbon may be deduced. This quantity, added to that obtained by burning the gases over oxide of copper, gives the total quantity of carbon contained in the iron. In drying the insoluble residue previous to combustion in oxygen, an elevated temperature must be carefully avoided; in fact, the safest way is to dry over sulphuric acid. The presence of hydrocarbons in the graphitic residue shows that this process cannot be safely applied for the estimation of combined carbon directly.

Weyl's very ingenious method for the estimation of the total carbon is founded upon the fact that a piece of iron, attached to the positive pole of a galvanic battery, and suspended in hydrochloric acid, is dissolved, while the hydrogen is given off at the negative pole. The formation of hydrocarbons, and a consequent loss, is in this manner prevented. One great advantage in this method is that the iron does not require to be in powder. A piece of iron 2 to 4 grammes in weight, attached to the positive pole of a Bunsen's cell, is suspended in dilute hydrochloric acid, just below the surface of the liquid. From the negative pole hydrogen passes off, while the iron dissolves quite quietly, and the strong solution of protochloride of iron formed may be seen falling in a regular stream through the lighter liquid. The iron is dissolved in about twenty-four hours, and the carbon is left behind in the same shape as the piece of metal from which it was derived. In Weyl's earlier experiments it was found that some of the liberated carbon at the positive pole was carried over to the negative pole by the mechanical working of the stream. To prevent this, a diaphragm of bladder or parchment paper is interposed between the two, which entirely obviates the possibility of loss in this way.

Mr. Tosh uses a small platinum sieve in which to lay the pieces of iron wholly immersed in the acid, and the action proceeds till the end as well as it does at the commencement. Any interruption of the current is not to be feared, as both amorphous carbon and graphite are good conductors of electricity. In this process there is always a slight loss of iron, owing to a slight evolution of hydrogen, which always takes place from the piece of iron during solution. This evolved hydrogen possesses the characteristic odour due to the presence of hydrocarbons, always noticeable when cast-iron is dissolved in acids under ordinary circumstances. When no more hydrogen is given off at the negative electrode, showing that all the iron is dissolved, the carbon is collected in a small funnel stopped with asbestos, dried cautiously, transferred to a platinum boat, and burned in a stream of oxygen, and the resulting carbonic acid is absorbed in the ordinary way by potash solution.

Weyl has proposed a second method for the solution of iron without the evolution of hydrogen, which consists in suspending a piece of the metal in dilute sulphuric acid containing bichromate of potassium dissolved. The

carbon is unaffected, and when most of the iron is removed, the residue may be collected and burned in oxygen.

The galvanic process was, we believe, first employed by Mr. Binks many years before Weyl published it. In a paper read before the Society of Arts in 1857, Mr. Binks describes a new method of analysing iron in the following words:—"The best malleable iron, on the one hand, and by way of comparison with this, the same kind of iron fully converted by the usual process, were taken on trial; the steel was dissolved in a very dilute and pure hydrochloric acid, and after many trials it was found best to place the bar of steel or iron in single voltaic arrangement with platinum, and to effect the solution in the cold with the usual precaution of expelling air from the water employed. In this way, slowly, the steel was dissolved, and the carbonaceous flocculent matter that was left collected, carefully dried, and analysed. The iron was treated in the same manner, and the comparatively very small proportion of carbonaceous residue given by it also examined. And these were compared with the residue obtained also from cast-iron. If the acid be strong, and heat be used, and the voltaic arrangement be not used, the results are very different. Gaseous nitrogen, in very minute quantity, is given off along with the hydrogen, some muriate of ammonia is formed in the solution, and but little nitrogen left in the residue."

Boussingault dissolves the iron by means of a solution of bichloride of mercury, which transforms the iron into protochloride, without there being the least evolution of a gas capable of carrying off or uniting with the carbon. The powdered iron is mixed with fifteen parts of bichloride. Add rapidly enough water to form a thin paste, and triturate for about half an hour in an agate mortar (when there is no objection to the introduction of a little silica, a glass mortar may be used). The diluted paste is introduced into a hard glass flask, and kept for an hour at a temperature of 80° or 100° C. Then throw it on a filter and wash with warm water. The protochloride of mercury containing the carbon, after being well dried in a water-oven, is put into a platinum boat and introduced into a glass tube communicating with a generator of dry hydrogen. Heat gradually up to a red heat in the current of gas. The protochloride is volatilised without decomposition. The volatilisation of the protochloride may equally well be effected in a current of nitrogen; but independent of the fact that it is not easy to keep up a sustained current of this gas, there will always be a suspicion of the presence of a little oxygen. In this respect hydrogen offers more security, especially if the device is employed of passing the dry hydrogen over a column of spongy platinum before it arrives at the tube containing the boat. The sponge retains the arsenic, and determines the disappearance of the oxygen which the hydrogen gas might contain. In proportion as the protochoride of mercury disappears, the presence of carbon becomes manifest.

Allow the boat to cool in a current of hydrogen, and then weigh it with the usual precautions. The carbon is voluminous, and of a fine black colour; it ignites and burns like tinder if the boat is heated a little. This is generally the case with carbon extracted from white iron, wrought-iron, and steel. The graphite coming from grey cast-iron only burns with the assistance of pure oxygen. The carbon leaves an ash after its combustion. Before weighing this residue it must be heated red-hot in a current of hydrogen. The silica of this ash when it comes from steel or wrought-iron, in which it cannot be supposed to come from scoria, comes from silicide; but it does not represent the totality of this because the silicium in combination with the iron, being first transformed into chloride by the bichloride of mercury, passes by the action of water into the state of silica, of which one part, being soluble, is carried away in the washings, while another part, insoluble, is left with the protochloride of mercury. It is this insoluble silica which is found after the combustion of the carbon.

The metallic substances submitted to the action of bichloride of mercury should be reduced to powder. There is no difficulty in this in the case of white cast-irons, for they pulverise easily. But when grey cast-irons, steel, and especially wrought-irons, are operated on, recourse must be had to the file to divide them, and this is an inconvenience which every one has experienced.

B. Estimation of the Graphite.—The employment of iodine and water for dissolving the iron and leaving the carbon has been recommended by some, and the weight of the carbonaceous residue obtained was thought to afford an approximate indication of the amount of carbon. But for this purpose it is necessary to dry the carbonaceous residue under the air-pump, or at a temperature of 120° to 130° C. Dr. Eggertz has shown that the quantity of carbon thus obtained is too great, though the weight of the residue is constant. He has also found that the residue contains iodine and water. To ascertain whether the quantity of carbon in the residue so obtained is uniform, he has burnt the residues from several different kinds of pig-iron and hard steel, and finds that the average amount of carbon is 59 per cent. Other analyses of the residue obtained from white pig-iron (free from graphite) gave as a mean result, after deducting the silica, the following as the composition of the carbonaceous residue:—

Carbon	59·69
Iodine	16·07
Water	22·50
Nitrogen	0·13
Sulphur	0·23
Loss	1·38
	100·00

The variation in the amount of carbon in four analyses was 0·5 per cent. The amount of carbon in the residue being taken as 60 per cent, since the quantity of this residue may vary to the extent of 1 per cent, owing to the different amount of sulphur in iron, the error in the estimation of carbon in steel containing 2 per cent carbon would not amount to more than 0·03 per cent. The carbonaceous residue does not change in weight when heated from 95° to 110° C.; but it loses 9 per cent by heating to 150°, and about 33 per cent by heating to 240°. Heated for a long time in a water-bath with hydrochloric acid, its character seems to change, iodine and water being disengaged, and oxygen absorbed.

Dr. Eggertz's method of estimating the graphite in iron and steel is as follows:—One gramme of iron reduced to small pieces, or white pig-iron crushed in a steel mortar, or grey pig-iron in small chips, is mixed with 5 grammes of pure iodine and 5 c.c. of water in a small flask, covered with a watch-glass, and placed in ice-cold water before adding the iron. It is to be kept for twenty-four hours at 0° C., and frequently stirred meanwhile. By keeping the liquid cold, no carburetted hydrogen is produced. The greater the amount of silicon in the iron the greater is the tendency to the production of carburetted hydrogen. The residue of carbon and silica left after the iron is dissolved is collected on a filter of known weight, when it is dried at from 95° to 100° C., washed thoroughly with hot water. After twelve hours, it is to be washed with a mixture of hydrochloric acid and twice its volume of water, heated to 70° or 80° C., until the filtrate ceases to give a blue colour with ferrocyanide solution. The object of leaving the residue for twelve hours is to allow any small particles of iron, remaining undissolved by the iodine, being oxidised by atmospheric air, and prevent disengagement of hydrogen when the hydrochloric acid is added. After the hydrochloric acid is washed out of the filter, it is dried with its contents at 95° to 100° C., until constant in weight. This weighing gives the amount of the carbonaceous residue and silica (but not the whole of the silica, because some part of it would have been dissolved), and by burning the carbon away and weighing the silica the weight of the carbonaceous residue may be ascertained. The carbonaceous residue may consist either of graphite or of the compound of carbon, iodine, and water already mentioned, if the carbon was combined with the iron. To ascertain which is the case, 1 gramme of iron is dissolved in 15 c.c. of hydrochloric acid (1·12 density) in a flask covered with a watch-glass, and, when the iron is dissolved, the solution boiled for half an hour. All the carbon combined with the iron is disengaged in the form of carburetted hydrogen gas, while the graphite and silica remain. If the carbonaceous residue, left after dissolving the iron, comes in contact with atmospheric air before the liquid is boiled, it is so altered that it is not dissolved and disengaged as gas. The

graphite that remains after boiling the liquid is collected on a filter of known weight, washed, dried, and weighed. It is then burnt, and the residual silica weighed to ascertain the quantity of graphite. Very satisfactory results have been obtained by this method. The differences do not amount to more than 0·1 per cent. When the quantity of carbon to be estimated is very small, more than 1 gramme of iron must be used in the analysis.

The following plan is simpler than the above, and may be used when only the graphite is required. In a beaker of 100 c.c. capacity mix 4 c.c. of sulphuric acid and 20 c.c. of water, and when the heat produced by the combination of the water and the acid has entirely disappeared, shake 2 grammes of finely powdered pig-iron into the dilute acid and boil for half an hour. (For steel and wrought-iron not less than 3 grammes should be taken, and the acid for solution increased in proportion). The solution is then evaporated until it measures 18 c.c., allowed to cool down to the temperature of 50° C., and 4 c.c. of nitric acid, sp. gr. 1·20, added; boil for a quarter of an hour, and allow to evaporate on a water-bath, until, on holding a watch-glass over the beaker, there occurs upon it no perceptible condensation. To the dry mass add 30 c.c. of water and 5 c.c. of hydrochloric acid, sp. gr. 1·16, boil for a quarter of an hour, and add more hydrochloric acid if there appears to be anything besides silica and graphite remaining undissolved. The insoluble silica and graphite are thrown on a filter, which has been dried at 100° C. and carefully weighed, washed with cold water until the washings give no iron reaction when tested with ferrocyanide of potassium; then washed with boiling water containing 5 per cent of nitric acid. The silica and graphite are then dried on the filter at 100° C., and weighed, ignited in a porcelain crucible, and the weight carefully taken. The difference between the weighings before and after ignition gives the amount of the graphite.

Mr. Tosh gives the following process for the estimation of graphite. 2 to 3 grammes of iron are treated with dilute hydrochloric acid, and when the solution approaches completion a considerable quantity of strong acid is added to separate the last portions of iron and manganese. The insoluble matter, consisting mostly of graphite, is collected on a carefully weighed filter, washed with hot water, dilute hydrochloric acid, solution of caustic soda, and hot water again, successively, and lastly with alcohol and ether to remove oily hydrocarbons. (By washing with dilute acid and with alkali, the iron and silica or oxide of silicon are separated). After drying at 120° C., the filter and graphite are weighed, and burned away. The small residue (a mere trace of silica or titanic acid) is weighed, and this weight subtracted from the first gives the amount of graphite. The results obtained agree very closely.

In washing the graphite with solution of soda, there is always a brisk effervescence, due to the oxidation of oxide of silicon to silicic acid, by decomposition of water, with consequent liberation of hydrogen.

C. Estimation of Combined Carbon.—When steel, or pig-iron containing carbon in chemical combination, is dissolved in nitric acid, a soluble brown colouring matter is formed, whose colouring power is very intense, and the solution assumes a tint which is dark in proportion to the quantity of the chemically-combined carbon. Iron and graphite (or free carbon) do not influence this colouration; for the solution of nitrate of iron is colourless, or, at most, slightly greenish, unless extremely concentrated, and graphite is insoluble in nitric acid.

Thus, in dissolving two pieces of different steels of the same weight in nitric acid, taking care to dilute the darker solution until the two liquids present exactly the same colour, it is very evident that the more highly carburetted steel will furnish the larger quantity of liquid, and that the proportion of the volumes will indicate the relative proportion of colour in the two steels. If now the composition and content of carbon of one of the steels is known, the absolute percentage of carbon in the other steel may be immediately deduced. Dr. Eggertz has applied these reactions to a method of estimating the combined carbon. To obtain trustworthy results certain precautions must be taken.

In a cylindrical test-tube, dissolve gradually in the cold, 10 centigrammes of wrought-iron, steel, or cast-iron reduced to a fine powder, in 1½ to 5 c.c. of nitric acid of 1·2 sp. gr. The use of nitric acid containing hydrochloric acid must be avoided, because the solution of iron would have a yellow tint. In proportion as the metal contains more carbon, more nitric acid must be used. After some time, when the chief part of the metal appears to be attacked, place the tube in a water-bath, and warm it to 80° C., in such a position that only the lower part of the tube is in contact with the warm water; a movement takes place in the acid, which favours its reaction upon the metal; a slight disengagement of carbonic acid from all the particles of carbon may be observed. The operation should always be conducted under the same circumstances as to heat and length of time. The evolution of gas having ceased (in operating upon steel, the reaction must continue two or three hours), place the tube in a large vessel filled with water, to bring the solution always to the same temperature. This precaution is indispensable, because the same liquid is darker when warm than when cold. Afterward, pour off, as exactly as possible, the clear liquid into a graduated burette. Upon the black residue remaining in the tube, pour some drops of nitric acid, and heat carefully over a lamp. If there is no further liberation of gas, the residue consists of nothing but graphite or silica. Cool the new solution, and add it to that which is already in the burette.

The liquid is then diluted with water until its colour corresponds exactly with that of the normal liquid, which latter should be of such a degree of concentration that each c.c. represents 0·0001 grm. of carbon. If, for instance, this normal liquid is prepared from cast-steel containing exactly 0·85 per cent of carbon, 1 decigramme of that steel must be dissolved in 8·5 c.c. of nitric acid; 100 grms. of steel containing 85 centigrammes of carbon would thus be dissolved in 8500 c.c. of the normal solution, 100 c.c. of that solution would represent 1 centigramme of carbon, and, consequently, 1 c.c. of the normal solution would represent 0·0001 grm. of carbon. To compare the normal solution with the solution of iron under examination, it should be contained in a tube of the same kind, and when the two tubes are held together by daylight before a thin sheet of paper, the colour should be exactly the same in both of them. As the normal solution alters slightly in colour by keeping, and begins to become paler after twenty-four hours, it is not possible to keep such a solution for use in a tube hermetically sealed. A solution of burnt sugar* in weak alcohol gives a solution of exactly the same shade of colour as the normal solution, and maintains its colour for a considerable time when protected from the light. But the best plan is to make the solution fresh, as it is required, by dissolving 0·1 gramme of steel, containing a known amount of carbon, in 5 c.c. nitric acid, and diluting it to the requisite degree, which may be indicated by a mark upon the tube corresponding to the percentage of carbon in the steel. If an iron solution exactly the same colour as the normal solution is diluted with one-tenth its bulk of water, the colour becomes distinctly paler, so that the delicacy of the method may be judged of from this.

Several modifications of this method have been proposed. The most successful of them, affording exceedingly accurate results, was communicated to the "Journal of the Franklin Institute," for May, 1870, by J. Blodget Britton, and has been tested for a considerable time. Instead of a single tube, containing a standard solution for comparison, as suggested by Eggertz, a number of tubes having their solutions differently standardised, one from the other, are employed. These are arranged securely in a wooden frame, with spaces between for placing the tube containing the solution to be tested, and forming together a convenient portable instrument called a colorimeter—a representation of such an instrument being shown in the annexed cut. The position of the tube containing the solution to be tested is shown at A. The tubes are ⅝ths of an inch in diameter, and 3¼ inches in length, filled with water and alcohol coloured with roasted coffee, and hermetically sealed. The solution in the tube to the left has its colour to correspond exactly with one produced by 1 grm. of iron, containing

* Slightly burnt sugar gives a yellow solution; highly burnt sugar gives a brown solution, but by mixing these solutions the right colour may be obtained.

0·02 per cent of combined carbon, dissolved in 15 c.c. of nitric acid. The solution in the tube next to it has its colour to correspond with one produced by the same quantity of iron, but containing 0·04 per cent of combined carbon, and so with each of the other tubes, increasing 0·02 per cent of carbon in regular succession to the right, the last reaching 0·3 per cent, as indicated by the figures on the upper rail of the instrument. On the back of the instrument, and for the purpose of partially screening the light and allowing the different shades of colour to be distinctly discerned, there is tightly stretched between the rails some fine white parchment paper. This screen is not shown by the cut, but it serves a very important purpose. The process is conducted as follows:—1 grm. of the finely divided metal is put into a tube of about 1½ inches in diameter and 10 inches long, and digested for fifteen or twenty minutes in 10 c.c. of nitric acid of a little more than 1·20 sp. gr., free from chlorine. The solution is then cautiously poured into a beaker, and a small portion of metal, which remains undissolved and adheres to the bottom of the tube, is treated with 5 c.c. of fresh acid, exposed to a gentle heat till completely dissolved, and added to the other. The contents of the beaker, when sufficiently cool, are filtered through two thicknesses of German paper (not previously moistened, and of a diameter not exceeding 4½ inches) into a tube about 5 inches long and of precisely

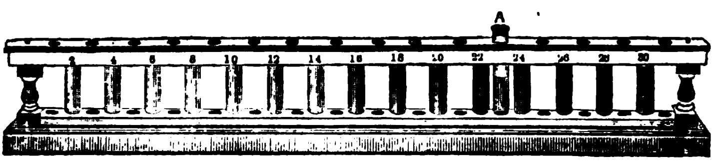


FIG. 1.

the same diameter as those in the instrument. After the filtered solution has remained for some minutes at the temperature of the atmosphere, and its colour become fixed, the tube is placed in the instrument and the carbon determined by a comparison of shades: the determination may be made readily as close as 0·01 per cent. Heat should not be applied in the first instance to facilitate the solution of the metal, because a high temperature is apt to cause a slight loss of colour. Two thicknesses of paper are taken because one alone is liable to break; and the paper should be used dry, for, if previously wetted, the water will weaken the colour of the solution; and it ought to be cut to a size not exceeding 4½ inches to prevent undue absorption. If the metal to be examined contains more than 0·3 per cent of carbon, 0·5 grm., or less of it, may be taken, or the solution may be diluted with an equal volume or more of water and the proper allowance made; or an instrument of higher range may be used. On the other hand, if the metal contains a very small percentage of carbon, 2 grms. of it may be

taken. For preparing the standard solutions (the normal ones begin to lose colour after some hours), caramel dissolved in equal parts of water and alcohol, as suggested by Eggertz, answers well; but with roasted coffee as the colouring matter the true shades may be obtained.

Estimation of Sulphur in Iron and Steel.

The plan usually adopted is to dissolve a weighed quantity (about 3 grms.) of the metal in strong nitric acid, adding a little hydrochloric acid occasionally, and evaporating the solution to dryness. Dissolve the residue in very dilute warm hydrochloric acid, and precipitate the sulphuric acid in the solution by means of chloride of barium. If the precipitated sulphate of barium, after washing once or twice by decantation, has a yellow or brown colour, owing to the presence of iron mechanically carried down, heat it, before filtering, with dilute hydrochloric acid.

Mr. H. B. Hamilton dispenses with the direct oxidation of the sulphur with nitric acid and evolves it as sulphuretted hydrogen, which is more easily oxidised. A weighed quantity of iron in a fine state of division (for puddle bars not less than 10 grms.) is thrown into a capacious flask, about an ounce of water is added, and the whole agitated to prevent caking in the after process. A cork is inserted into the mouth with two perforations, the one for a safety funnel tube to admit acid, the other for a tube bent at right angles. The latter tube communicates with a U-tube, containing a solution of caustic potash free from sulphate. Either concentrated hydrochloric acid or water are to be poured in at the funnel, according to circumstances. As soon as the action, after pouring enough hydrochloric acid into the flask, has almost ceased, the contents of the latter are to be boiled. The flame is then taken away, and, as soon as the ebullition has ceased, air is sucked through the apparatus for about a minute. This process may be repeated, if, as will easily be discovered, the action of the acid has not entirely ceased. The contents of the U-tube are emptied into a beaker, and the tube rinsed out with distilled water. A current of chlorine is allowed for some time to pass through the solution, which is then boiled, acidulated with hydrochloric acid, and boiled again, to drive off all hypochlorous acid, when it is precipitated with chloride of barium. The contents of the flask are filtered through asbestos, and, without washing the residue at all, it is transferred again to the flask, removing every particle from the funnel by means of a small quantity of nitro-hydrochloric acid. After heating, in order to oxidise the black residue with the nitro-hydrochloric acid, water is to be added, and some carbonate of soda, free from sulphate, to neutralise the large excess of acid. After boiling, filter, taking care that the solution is still slightly acid; precipitate with chloride of barium, add the solution with precipitate suspended in it to the former one, and proceed in the usual manner.

Dr. Eggertz, to whom analytical chemistry is indebted for the colorimetric process of estimating combined carbon in iron and steel, has devised an equally expeditious plan for estimating the sulphur. He takes one decigramme of cast-iron, wrought-iron, or steel, cut up or pulverised, and passed through a sieve with holes not larger than 0·6 m.m., and introduces it by means of a glass or glazed paper funnel, into a flask about 0·15 metre high and 5 centimetres diameter, previously containing 1 grm. of water and 0·5 grm. of concentrated sulphuric acid; or, in preference, 1·5 grm. of sulphuric acid, sp. gr. 1·25, and whose volume (1·5 c.c.) has been marked on the flask. A piece of polished silver plate (18 m.m. long, 7·5 m.m. wide, and 1 m.m. thick, with a hole at one end), composed of 75 per cent of silver, 25 per cent of copper, and attached to a thin platinum or silver wire, is quickly introduced into the flask, so that it may be a little below the neck; a cork is put in so as to hold the wire without completely closing it. It is allowed to stand fifteen minutes at the ordinary temperature, and the silver plate is then removed. If the iron contains sulphur, the plate is coloured by the sulphuretted hydrogen gas disengaged during the solution of the iron in the dilute sulphuric acid; and, according to the amount of sulphur present, the colouration of the plate passes to a coppery yellow, a bronze brown, a bluish brown, or a blue. These colourations are determined with the greatest accuracy—especially that of the silver plate alone, No. 1; that of coppery yellow, No. 2; that of bronze brown, No. 3; that of blue, No. 4. The intermediate degrees may be represented by decimals, thus: 2·5 if the colouration is between 2 and 3; 3·1 if the plate is one-tenth towards the blue; 3·5 if it is as much blue as brown; 3·9 if the brown colouration is feeble.

As the normal colouration No. 2, Dr. Eggertz has adopted that of the bronze called yellow metal, newly rubbed with fine sand on leather. (This metal consists of 60 parts of copper and 40 of tin.) For the colouration No. 3, a convenient alloy has not yet been found. A bronze, consisting of 85 parts of copper and 15 parts of zinc, does not quite represent the colour which should be obtained, for when freshly cleaned it is too bright, and at last takes a bluish colouration. For the colour in question it is better to use a plate of silver which remains in the flask during the solution of the iron, until it has become as brown as possible, and a slight bluish colour begins to be perceived; the plate is then removed and preserved in a well-closed tube. The colour No. 4 resembles that of a watch-spring. If the amount of sulphur is very considerable, this colouration passes to a clear bluish grey. By passing the plate of silver over a bottle of sulphide of ammonium the desired number can be easily obtained. To obtain in these assays for sulphur the proper tint on the silver plate, it is necessary to take certain precautions. The plate is to be held in pincers and cleaned

as well as possible by rubbing it with a soft leather on which is placed a little very fine rotten-stone. Contact with the fingers is avoided by means of a piece of paper, and the plate is to be carefully dried with a piece of filtering paper. If the plate, by cleaning or by the action of the burnisher, has been purified on its surface, this should be carefully removed by again rubbing with the leather, for pure silver is less sensitive to the action of the gas than that of the given standard. Thus it has sometimes been found that the silver employed for coinage furnishes less homogeneous plates, of which those parts richest in copper assume more quickly the blue colouration. On this account, the plates should be compared between themselves, by introducing them at the end of a wire into a flask in which iron is dissolving containing from 0·05 to 0·08 per cent of sulphur. On introducing the plate, care must be taken not to turn the side but the edge against the strongest current of gas, which would otherwise colour one face of the plate stronger than the other. The plate should be rapidly introduced into the flask after the introduction of the iron, as then a very strong disengagement of sulphuretted hydrogen immediately takes place. After a first experiment the flask is to be filled with water several times, so as to get rid of the odour of sulphuretted hydrogen. If a steel mortar is employed to pulverise the iron, the whole of the piece selected should be reduced to a very fine powder. The mortar should be well cleaned each time, taking care to remove the disc from the bottom. Changes in temperature between 15° and 25° C. seem to have no sensible influence on the colouration of the metal; if the temperature exceeds 40° the plate becomes moist and gives false indications. Some practice is required to judge of the colouration of the plate, but it may be easily acquired. Generally the best plan is to place the standard plates of tints 1, 2, 3, &c., on a sheet of white paper by the side of the plate under experiment, exposing them to a good light near a window (but not sunlight), and to examine them with a lens. The colourations between 2 and 4 are the most difficult to recognise; but with a little experience, none will vary more than 0·1, so that, for instance, the colouration may be estimated between 3·5 and 3·6.

The following is somewhat an approximation between the different colourations upon the silver plate, and the amount of sulphur in a great number of different samples of iron :—

Number of the Colouration.	Percentage of Sulphur.
1·0	0·00
1·2	0·01
2·0	0·02
2·5	0·03
3·0	0·04
3·1	0·05

Number of the Colouration.	Percentage of Sulphur.
3·2	0·06
3·3	0·07
3·5	0·08
3·6	0·09
3·7	0·10
3·8	0·12
3·9	0·15
4·0	0·20

It is evident that in this way the exact quantity of the sulphur is not determined; but several years' experience have shown that if these experiments are made with care, and the quantity of sulphur does not exceed 0·1 per cent, the results are near enough for all practical purposes. Iron which does not colour the silver plate will sometimes produce a colouration if we double the quantities of iron and acid. With half the quantities of acid and sulphurised iron, silver generally gives a little more than half the real quantity of the sulphur which is present.

Amongst experiments on the estimation of sulphur in iron, the following deserve mention:—1. The quantity of sulphur in wrought-iron is often so small that it produces no colouration on the silver plate; this iron, therefore, not being red-short, may be employed for all kinds of uses. It must not, however, be forgotten that the quantity of sulphur is not equally distributed throughout a piece of iron, but that it may vary considerably in different places. On experimenting with the turnings obtained from a portion of an iron bar which was visibly red-short, a stronger tint is often obtained on the silver plate than when using other parts of the bar. The fragments obtained from red-short iron in boring a horse-shoe do not often give on the silver plate a deeper colouration than 2, and it appears to follow that ordinary wrought-iron which contains 0·02 per cent of sulphur in certain parts cannot conveniently be employed for this purpose. If the red-short iron gives to the plate a slighter and more feeble colouration than 2, it may be supposed that the breaking is due less to sulphur than to an insufficient working of the cast-iron, the crude pieces in wrought-iron entirely free from sulphur often acting as if they were red-short. In general it appears certain that the quantity of sulphur in iron is more injurious when the iron has been badly worked. In a hard iron melted in a steel crucible, we may, in spite of its containing 0·04 per cent of sulphur, make holes like those in a horse-shoe without any trace of cracks, which may undoubtedly be attributed to the homogeneousness and good working of this iron; the quantity of phosphorus being only 0·03 per cent. The lower portion of an English rolled rail, without fault, contained 0·11 per cent of sulphur and 0·3 per cent of phosphorus; a portion was cut off which was so red-short that it could not be made use of.

2. The richness in sulphur of steel of the best quality is such that the colourations on the silver plate vary only between 1 and 1·5. As in the case of wrought-iron, the quantity of sulphur often varies in different parts of the same piece of steel, and that also appears to be the case in a little less decided manner in cast-steel.

3. The quantity of sulphur in cast-iron is rarely so little as not to colour the plate. In the greater number of Swedish cast-irons, this quantity is such that the silver plate varies in colouration between 2 and 3. In iron for gun castings it is between 3·3 and 3·7, and sometimes more. In cast-iron the quantity of sulphur is often distributed unequally; there is generally more on the surface than is met with below. If the colouration of the silver plate does not exceed 3, we can assume that the cast-iron refined in the ordinary manner will not give red-short iron, especially if the refining is done carefully. But as in different methods of refining different quantities of sulphur may be removed from the iron, and, in general, more if the iron is the result of a light charge of the blast furnace, it cannot be said beforehand that all cast-iron, which communicates a bluish colouration to the plate will necessarily give red-short iron. This will be the case, however, with cast-iron which colours the plate as deep a blue as that of a watch-spring. In cast-iron, which gives a red-short wrought-iron, without rendering the silver plate more than brown, it is probable (the iron having been well refined) that the cause is owing to the presence of other substances than sulphur, but this occurrence is very rare. Many circumstances appear to show that the quantity of sulphur in iron diminishes with time, at least on the surface, and under favourable conditions.

The quantity of sulphur in a mineral cannot be estimated in the manner just described; all that can be done is to estimate the sulphur in the cast-iron, which is obtained by reducing the mineral in a crucible. Attention must always be paid to the following:—*a*. That the powdered charcoal which fills the crucible is free from sulphur. This is ascertained by fusing iron, as free as possible from sulphur, in a crucible filled with the same powdered charcoal, and then examining the regulus obtained. If this latter gives a higher amount of sulphur than the iron originally contained, the cause is attributable to the charcoal. At Fahlun, the charcoal absorbs, in a short time, much sulphur from the smoke of the burning pyrites; and the powder selected for the crucible experiments in the Mining School is obliged to be kept in closed vessels. If the charcoal employed as a combustible in the crucible furnace is exposed to the action of much sulphuretted hydrogen or sulphurous acid, the experiments show it. *b*. The state of the mineral, whether unroasted, badly roasted, or well roasted. The small laboratory experiments, having for their object to ascertain how much sulphur can be removed from a mineral by roasting in bulk, are always inexact. *c*. The

influence exerted on the quantity of sulphur by the minerals mixed with it. It follows, from many experiments made at the Mining School, that the more silicic acid the slag contains the more sulphur the cast-iron receives, and that the quantity of sulphur gradually diminishes in proportion as the quantity of lime is increased. In general, assays for sulphur should be made with regulus obtained from a mixture containing as little lime as possible, but giving vitreous slags. If the colouration of the silver plate does not exceed No. 3, the quantity of sulphur may be considered as insignificant, especially in experimenting on non-roasted minerals.

The lime used in blast furnaces may be assayed for sulphur in the following manner:—Mix 0·8 gramme of rich and pure iron mineral with 0·2 gramme of quartz and 0·2 gramme of lime; fuse the mixture as usual in a crucible, and assay the resulting iron for sulphur. In this manner it may be ascertained if the lime contains an injurious dose of sulphur. If it were chemically pure we should obtain, by the addition of 2 or 3 per cent of clay or talc, free from sulphuric acid, a better slag. If, on the contrary, the lime contains much silicic acid, more than 0·2 gramme should be taken for the experiment.

Estimation of Sulphur in Iron Ores.

Five grammes of the mineral, ground as finely as possible in an agate mortar, are treated with chlorate of potassium and hydrochloric acid. After desiccation and extraction with hydrochloric acid and water, the insoluble substances may be sulphates of lead, calcium, barium, and strontium, silica, and undecomposed mineral. By stirring well and filtering the liquid whilst warm, the two former salts may generally, however, be dissolved. The filtration should be performed through a double filter, to prevent the pulverised mineral from passing through. When the clear portion of the solution has been poured upon the filter, add to the insoluble matter 5 c.c. of hydrochloric acid and 5 c.c. of water; then leave the mixture for two hours on the water-bath at a boiling temperature, when, if care be taken to stir well, the sulphate of calcium will be completely dissolved. Wash the insoluble portion in warm water, and pour it on a filter, taking care to place below a flask specially to receive that portion of mineral which may have passed through the filter. The filtered liquid, whose volume is about 50 c.c., should be rapidly boiled and mixed with 2 c.c. of a saturated solution of chloride of barium. (This amount is sufficient to precipitate the sulphuric acid formed from 0·1 grm. of sulphur.) After cooling add to the mixture 5 c.c. of ammonia, sp. gr. 0·95, then stir well with a glass rod, and leave the whole to rest at the ordinary temperature for twenty-four hours. The clear solution should be decanted as completely as possible on to a strong filter, and the precipitate stirred up with about 20 c.c. of cold

water, and then left to itself until it has quite settled. If warm water is used without having added a few drops of hydrochloric acid, a little oxide of iron will precipitate. The clear liquid is likewise thrown on to the filter, and the operation is repeated several times with cold water, and then two or three times with boiling water, without which precaution the sulphate of barium will pass through the filter. Finally collect the precipitate, and wash it with warm water. The last drops of this water, on being evaporated on a watch-glass, ought not to leave more than a scarcely visible white ring. The precipitate is then dried, heated to redness, and weighed. If it is coloured with oxide of iron it must be washed with a little hydrochloric acid, dried in the water-bath, and taken up with a few drops of acid and water, and then the preceding operation repeated (washing, drying, heating, and weighing). If the precipitate has only a feeble red colour, which is often the case, this latter operation will be unnecessary.

To dissolve the sulphate of lead which may occur in the insoluble portion, remove this from the filter with the end of a feather, introduce it into a flask, and pour over it 10 c.c. of concentrated acetate of ammonium. The solution, after having been strongly agitated and heated in the water-bath, is carefully poured on to a filter. Then wash the residue with a little acetate of ammonium, and repeat the treatment until a few c.c. of solution, acidulated with a little acetic or hydrochloric acid, is not rendered turbid when warmed with chloride of barium solution. The filtrate is then diluted, slightly acidified, and the sulphuric acid precipitated by means of chloride of barium. After the sulphate of lead has been removed, there may still occur sulphates of barium and strontium in the insoluble portion. To decompose these salts the residues must be dried, heated to redness, and weighed, and then fused with five times their weight of pure dry soda. The mass is digested with water over a water-bath, the liquid filtered, and the residue washed with warm water. The silicic acid is separated from the solution, which contains the silicate, the carbonate, and the sulphate of sodium, by adding hydrochloric acid and drying on the water-bath. After filtering, precipitate the solution with chloride of barium. To ascertain if the iron mineral contains gypsum or other soluble sulphates, take 5 grammes, place them in 20 c.c. of hydrochloric acid and 60 c.c. of distilled water, and digest them for three hours on the water-bath, with frequent agitation. The filtered solution is mixed with chloride of barium and 15 c.c. of ammonia; then proceed as already described. If there are present in the mineral grains of iron- or copper-pyrites, or galena, they will only give traces of sulphuric acid in this operation.

To ascertain the accuracy of the process which has just been described, the following experiments were made by Dr. Eggertz.

Experiment I.—Sulphide of iron (as usually employed in the preparation

of sulphuretted hydrogen) was dissolved, as above described, in hydrochloric acid, water, and chlorate of potassium, in a flask furnished with a glass tube leading into a solution of sulphate of copper. No trace of precipitate, nor any colouration which would indicate the presence of sulphide of copper, could be detected in the solution; so that it is certain that no loss of sulphur could take place on dissolving iron or minerals in this manner. When the experiment was repeated, but with this modification, that the solution of chlorate of potassium, during the addition of hydrochloric acid, was not kept well boiling, the sulphate of copper solution was rendered turbid, showing the necessity of resorting to complete ebullition.

Experiment II.—Sulphide of iron treated in the same apparatus with aqua regia (composed of equal parts of nitric and hydrochloric acids) requires a more equal temperature and a stronger ebullition to prevent any precipitation of copper. Moreover, as the solution of iron by chlorate of potassium takes place promptly, and as the presence of nitric acid is prejudicial both for the solution of the mass after drying in the water-bath (owing to the formation of subnitrate of iron), and also for the precipitation of the solution by chloride of barium, preference should be given to the employment of chlorate of potassium.

Experiment III.—One gramme of pure pyrites was treated in the manner above described, and the sulphur which separated at first was completely dissolved during the drying of the liquid on the water-bath. Upon precipitating with chloride of barium, a quantity of sulphate of barium was obtained, exactly corresponding to the amount of sulphur in the pyrites.

Experiment IV.—Many experiments were made with the filtered liquids obtained from solutions of iron which had been freed from sulphur by excess of chloride of barium. After standing for several days these have been brought to ebullition and mixed with 1 c.c. of an aqueous solution of sulphate of sodium, containing a quantity of sulphuric acid corresponding to 0·0001 gramme of sulphur. At the end of at least twenty-four hours a feeble precipitate is observed, which proves that the sulphuric acid is perfectly separated from the iron. This precipitate is rendered distinctly visible when the contents of the flask are stirred by moving a glass rod circularly round the liquid, for the sulphate of barium then mounts in a small whirlpool and falls again on to one spot. When, also, 50 c.c. of the solution of sulphate of sodium are added to the filtered liquids, the corresponding weight of sulphate of barium has been obtained. If, in the filtered liquids, there were 10 c.c. of free hydrochloric instead of 5, two days sometimes elapse before the precipitate from the solution (containing 1 c.c. of the sulphate of sodium solution) becomes visible. Consequently, if there are more than 5 c.c. of free hydrochloric acid in the solution, there must be added for each c.c. in excess (to the solution after addition of chloride of barium

and then cooling) 1 c.c. of caustic ammonia, so as to nearly neutralise the hydrochloric acid.

Experiment V.—In many experiments in which the sulphate of barium was washed for a long time on a filter, both with warm and cold water, it was impossible, upon evaporating a drop of the filtrate on a watch-glass, to avoid traces being left on the latter. Some drops of a solution of chloride of barium and a little hydrochloric acid having been added to the filtrate always produced a feeble white precipitate by the action of heat. For this reason the washing should only be continued until a drop of the washing water leaves, on evaporation on glass, an *almost* imperceptible white ring.

Experiment VI.—4·9 grammes of carbonate of calcium, and 0·1 gramme of pyrites submitted to the same process of solution gave, by evaporation on the water-bath, a perfectly clear liquid; after drying, 6 c.c. of hydrochloric acid and 50 c.c. of water were added to the residue, and there was thus obtained a considerable mass of gypsum. On leaving the liquid for an hour on the water-bath and increasing the quantity of water, the gypsum was completely dissolved.

One decigramme of gypsum was dissolved in 2 c.c. of hydrochloric acid and 4 or 6 c.c. of water (or better still in 10 c.c. of acetate of ammonium). The solution was left for half an hour on the water-bath with frequent agitation. It could then be diluted with water at pleasure, without the gypsum being precipitated.

Experiment VII.—0·5 gramme of galena was completely dissolved in the same manner, and the solution brought to dryness on the water-bath. A little water was added to remove the chloride of potassium, and evaporated after solution of this salt; the sulphate of lead which remained was then completely dissolved in 20 c.c. of acetate of ammonium, and precipitated with acetate of barium containing a little free acetic acid. The sulphate of barium, which was of the proper weight, was of a grey colour, but became whiter without alteration of weight by being heated to bright redness for some time with access of air.

One decigramme of sulphate of lead dissolves without rise of temperature in 2 c.c. of acetate of ammonium; chloride of lead dissolves in it still more easily. The solution may be diluted with water without any precipitation taking place.

One decigramme of sulphate of lead was dissolved on the water-bath by violent agitation for half an hour with 4 c.c. of hydrochloric acid (of 1·12 sp. gr.) diluted with 2 c.c. of water; but the sulphate commenced to crystallise as soon as the liquid was cooled to 60° or 70°.

Experiment VIII.—4·7 grammes of an iron mixture containing a known quantity of sulphur having been mixed with 0·1 gramme of pyrites,

0·1 gramme of sulphide of lead, and 0·1 gramme of gypsum, treated in the same manner as the iron mineral, gave exactly the quantity of sulphate of barium which it should have yielded by theory. The precipitate from the solution in acetate of ammonium only weighed a few milligrammes.

Experiment IX.—An aqueous solution of sulphate of sodium, accurately standardised, and then chloride of barium, were added to a solution of soluble glass acidulated with hydrochloric acid. The weight of the sulphate of barium which was formed showed that the gelatinous silicic acid dissolved in the acid does not interfere in these experiments.

Experiment X.—0·1 gramme of pure quartz was fused with 0·5 gramme of anhydrous soda in a platinum crucible. The mass was completely soluble, without heating, in 5 c.c. of water, and the liquid remained clear even in the water-bath.

Experiment XI.—0·1 gramme of sulphate of barium was fused in a platinum crucible with 0·5 gramme of carbonate of sodium; the mass, treated with water, was poured upon a filter and washed. The carbonate of barium remaining on the filter was brought to a red heat, and then dissolved in dilute hydrochloric acid without the least residue. The same experiment was tried with sulphate of strontium. It follows, therefore, that these two salts may be completely decomposed by fusion with carbonate of sodium.

Estimation of Silicon in Iron and Steel.

All who are occupied in the analysis of iron and steel are aware how very uncertain the determination of silicon is when the method hitherto used for its separation is followed, because cast-iron, and even bar iron and steel, are never found absolutely free from intermingled slag. This slag is decomposed by the ordinary method of dissolving the iron in acids, and its silica then augments the amount of silica formed from the silicon contained in the iron or steel. This cannot be said of every sort of cast-iron, but these sometimes contain blast-furnace slag, although pig-iron containing slag may be considered as rare. It ought also to be mentioned that crystallised silicon has been found in crystallised cast-iron from Krain, in the form of small silvery plates, which were neither acted upon by boiling aqua regia nor by ignition in oxygen gas; but they were converted into silica by fusing with carbonates of potassium and sodium.

Crystallised silicon is insoluble in hot solutions of carbonate of sodium, but is soluble, with development of hydrogen, in hot solutions of caustic potash, and also in hot hydrofluoric acid. The accurate determination of the silicon in iron and steel has been effected by Dr. Eggertz, who, after fruitless efforts to dissolve iron in highly diluted organic or inorganic acids, which should have no effect on the refinery slag, finally discovered such a

solvent in bromine, which, when mixed with water, dissolves the iron without the slightest action on the accompanying slag. But as experimenting with bromine in large quantities is very disagreeable, trials were made to use iodine instead; and this, like bromine, has been proved to have no effect on the slag, nor on the oxide or proto-sesquioxide of iron, or proto-sesquioxide of manganese. At the same time, bromine dissolves iron quicker than iodine, and is, perhaps, more easily obtainable in the requisite state of purity. Moreover, as continued experiments have shown that a solution of carbonate of sodium can separate finery slag from the silica which has been formed by the use of iodine or bromine on the silicon contained in the iron, the following method for the determination of silicon and slag in bar iron or steel has been used and considered successful; the same method may be employed for cast-iron, because blast-furnace slag, when such is found, is not perceptibly changed by iodine or bromine, nor by solutions of carbonate of sodium. Three grammes of bar iron or steel which has passed through a sieve of 0·2 of a line are taken for analysis. Fifteen grammes of iodine are added in small portions at a time to 15 c.c. of water in a beaker of 100 c.c. capacity. The water must be previously boiled to expel the air, which would otherwise oxidise the iron, The iodine is stirred in the water with a glass rod, in order to get rid of the air which has accompanied it, and the floating iodine particles are allowed to sink. The beaker with the iodine and water, which is kept covered with a watch-glass, is cooled in ice before the iron is put in, and during the solution it is kept at the temperature of 0° C. For the first few hours it must be well stirred every hour, or oftener, with a glass rod, but afterwards not so frequently. In consequence of the low temperature and the careful admixture of the iron (by which heat is prevented), the solution may be performed without the least development of gas, and the iron has less tendency to become oxidised by the air when at this low temperature. By pressure, and by agitating with the glass rod, the solution of the iron particles which collect at the bottom of the beaker is much facilitated; if no lumps of iron particles are visible, the beaker may be kept at the ordinary temperature, or, preferably, in ice water. If some of the solution has dried on the sides of the beaker or on the glass rod, it must be well moistened with the same solution before water is added. About 30 c.c. of water, which should be very cold in order to prevent the formation of basic salts, are added to the solution; it is then well stirred, left to settle, and the fluid with the lighter particles of graphite is poured on to a filter of 2 in. diameter; the filtration is kept up without interruption until there remains only a somewhat heavy dark powder of slag, &c., at the bottom of the beaker; about 5 c.c. of water, with a few drops of hydrochloric acid, are now poured in and stirred with the glass rod; if hydrogen is given off, it is

an indication that there is still some metallic iron undissolved. The acidified water is quickly poured on the filter, in order not to act on the slag. If a development of gas is perceived, a little iodine, with carbonate of sodium and water, is added for the complete solution of the iron, and the residue is thrown on the filter and washed with cold water, until a drop of the filtrate gives no reaction with a solution of 0·2 per cent of ferrocyanide of potassium contained in a small porcelain crucible. Solutions containing 0·00001 gramme of oxide of iron per c.c. show in this way very distinct reactions, particularly if a drop of dilute nitric or hydrochloric acid be added. The filtrate is evaporated to dryness, in which operation some of the iodine is sublimed away. Thirty c.c. of hydrochloric acid, 1·12 sp. gr., are then added, and it is again evaporated in order to obtain the silica which may be dissolved in it. The filter, previously dried and weighed, is again dried and weighed when containing the precipitate. It is then ignited, and the residue weighed. After ignition, the residue is boiled in a solution of soda, in order to extract the silica, and weighed. It should be observed that some part of the silica which has been formed from the silicon in the iron may possibly unite with the slag during the drying and ignition. In consequence of this, it is difficult to extract it by means of a soda solution, whence this method is not to be recommended in exact determinations of silicon.

When using bromine as a solvent, 6 c.c. must be taken to 3 grammes of finely powdered iron or steel, with 60 c.c. of water, which has been previously boiled, and cooled to 0° C.; and this temperature must be preserved by placing the beaker in ice water until the solution is complete, which usually takes place in two or three hours; it is cautiously stirred once or twice with a glass rod; if stirred hastily, the solution proceeds too violently. The further operations are conducted in the same manner as when using iodine. The bromine is most conveniently preserved under water, and is taken up by a pipette, which is introduced into the bottle, the upper end being kept closed by the finger.

When it is preferred to dissolve iron or steel in lumps instead of in powder, this may be done; but it is not then necessary to place the beaker in ice water, as the metal is less violently acted upon in this form. Several days are required for the solution; the iron, and particularly the steel pieces, must be occasionally cleaned from the graphite which adheres to their surface.

In order to determine the silica (formed from the silicon in the iron) and slag, the filter, which contains graphite (in combination with iodine or bromine and water), silica, and slag, is unfolded, whilst it is still wet, on a watch-glass. The contents are washed away from the filter (these should only occupy the lower half of the filter whilst in the funnel) with a very

fine jet from a wash-bottle (so as not to obtain too much water) into a platinum or silver crucible of the capacity of 30 c.c. The loosening of the mass may be facilitated by a fine camel-hair pencil. The water in the crucible is evaporated to about 6 c.c., then mixed with 3 c.c. of a saturated solution of carbonate of sodium, free from silica, and the crucible put in a water-bath. It is kept in the boiling water 1 hour, during which time the liquid is stirred two or three times, and the insoluble mass crushed with a platinum spatula. The supernatant liquid is carefully poured from the insoluble mass on to a small filter, and to the mass in the crucible are added 1 c.c. of saturated solution of carbonate of sodium and 2 c.c. of water. When this has been boiled 1 hour, the whole contents of the crucible are thrown on the filter and washed. The solution of silica in soda is acidified by hydrochloric acid, and mixed with the iron solution, and the whole evaporated to dryness on a water-bath. When the solution attains the thickness of ordinary syrup, it is stirred very often with the glass rod, until the mass becomes a dry powder, and heated until the smell of hydrochloric acid has nearly gone off; the beaker is then placed in boiling water for 6 hours, 15 c.c. of hydrochloric acid of 1·12 sp. gr. are then added, and the beaker left on the water-bath 1 hour. As soon as the red powder is entirely dissolved, 50 c.c. of water are added; and when no crystals of chloride of iron are visible, the solution is thrown on a filter and washed with cold water, warm water forming basic iron salts which make the silica appear red. The filter containing the silica is dried and ignited in a porcelain crucible, gradually increasing the temperature to a full red heat, and weighed; if the silica is coloured red by oxide of iron, a little hydrochloric acid, 1·19 sp. gr., must be poured into the crucible. One decigramme of ignited and pure silica obtained from analysis will dissolve in the above manner in 6 c.c. of a saturated soda solution and 12 c.c. of water. If any residue is observed after the second boiling, this arises from some impurity which has united in small quantities with the silica, rendering it insoluble. When strong hydrochloric acid is boiled with this insoluble silica, it may afterwards be dissolved. When the solution of silica is diluted with water to the volume of 50 c.c. at the ordinary temperature, it has no tendency to come into the form of jelly. Quartz powder is dissolved by the preceding method, but very slightly, but ignited titanic acid and finery slag are not acted upon, and the tersilicate slag from blast-furnaces but very little.

When the silica is quickly exposed to a high temperature, a considerable loss may arise from the spirting of the water combined with the silica. Silica dried at 100° C. has been proved to retain 1 equivalent of water to 3 equivalents of silica, that is, about 6 per cent of water, which is lost by a strong ignition. The oxide of iron is easily dissolved in the heat of a water-bath. The silica is again thrown on a filter, washed, dried, ignited, and weighed.

To ascertain the purity of the silica, it may be mixed in a platinum crucible with ten times its weight of pure fluoride of ammonium, diluted with water to the thickness of syrup. The water must be evaporated on a water-bath, and the crucible heated, with a cover on it, by a gradually increasing heat over a spirit-lamp to a full red. If nothing is left in the crucible, the silica was pure, and has passed off as fluoride of silicon; but, if anything remains, the operation with fluoride of ammonium must be repeated until a constant weight is obtained. When iron contains tungsten, some tungstic acid is formed, and this accompanies the silica for the most part, being dissolved by the soda solution, but it is not volatilised by the use of fluoride of ammonium. Vanadic acid also accompanies the silica, behaving as tungstic acid. Instead of using fluoride of ammonium, it is preferable to use hydrofluoric acid, with which the silica is moistened, and the evaporation is conducted on a water-bath. The mass left on the filter from the soda solution may be composed of—besides graphite—slag, oxide of iron, oxide of titanium, &c. (but not copper, at least when the iron does not contain more than 1 per cent); this is dried, ignited, and weighed. The method of separating oxide of iron and slag, when the iron or steel contains both these, is not yet known. If the composition of slag were always alike (which it is not) it would be easy to calculate its amount from either the silica or oxide of iron obtained in the analysis. In a piece of very red-short Bessemer iron which contained no sulphur, by several experiments 0·3 per cent of oxide of iron has been obtained, and only traces of silicon. After ignition, the oxide of iron may possibly be found as sesquioxide. The amount of oxygen, in case the red-shortness is due to this, as it probably is, amounts to less than 0·1 per cent.

When the iron or steel for analysis contains titanium, a part of this substance follows the slag in the form of titanic acid. If such is the case, this must be melted with ten times its weight of acid sulphate of potassium, by which it is dissolved; the mass is dissolved in cold water, and the solution precipitated by boiling; the weight is determined, and subtracted from that of the slag. (See Titanium, p. 46; also p. 104 and chapter on Silicates).

In respect to the determination of silicon in cast-steel where only a trace of slag is found, the method given below for cast-iron may be employed; but 3 grammes at least ought to be taken for each experiment, and the acids for solution in proportion. The amount of silicon in bar iron and steel generally varies between 0·01 per cent and 0·1 per cent; but in two sorts of good cast-steel from Krupp's it has amounted to about 0·3 per cent. Slag in cast-steel has been found only in traces, but in another case it amounted to 0·2 per cent; in good iron wire, prepared from bar iron, converted in a refinery hearth, from charcoal pig-iron, 0·33 per cent; in puddled iron (armour plate), from 0·75 to 3 per cent; and in an English iron rail, to 4 or 5 per cent.

For the determination of silicon in cast-iron, in which no finery slag is found, and only exceptionally blast-furnace slag, the following method has proved suitable:—2 grammes of iron, which has passed a sieve with holes of a diameter of $\frac{1}{80}$ inch at the most, is put into a beaker of 100 c.c. capacity, containing 30 c.c. of hydrochloric acid, sp. gr. 1·12. The beaker is covered with a close-fitting watch-glass, heated without delay, and the liquid kept in gentle ebullition for half an hour. All the carbon chemically combined with the iron is separated from the liquid in the form of an ill-smelling volatile hydrocarbon. If the carbon separated on solution is left in contact with the air some minutes before ebullition, it undergoes such a change that it does not go off in a volatile form; if necessary, some hydrochloric acid is added, and the solution evaporated to dryness on a water-bath. When the silica is red, strong hydrochloric acid is added, as previously described. If the silica is contaminated with titanic acid, vanadic acid, or tungstic acid, it is operated upon with fluoride of ammonium or hydrofluoric acid, as previously mentioned, whereby the silica is volatilised and calculated by loss. By the above method of dissolving iron in hydrochloric acid, the silicon changes, without evaporation, for the most part, to insoluble silica, which may be filtered and determined. Sometimes a very unimportant part is dissolved, especially if the boiling has been insufficient. When iron is dissolved in hydrochloric acid without heating (white cast-iron is very difficult to dissolve in this way), a still less portion of silicon is dissolved, and generally so little that it may be neglected for practical purposes. The washing is performed with hot water containing nitric acid, as previously described. When the iron is dissolved in nitric acid, a great deal of silica enters into solution. The different sorts of cast-iron appear to be slightly different in this respect. In dissolving cast-iron by the aid of heat, in very dilute sulphuric acid, a great deal of silica is dissolved, but very little when the acid is strong; as the water evaporates, the silica separates and becomes insoluble.

The method given below rests upon these circumstances, and has proved very satisfactory, whilst the removal of the acid is avoided, which is both necessary and troublesome when using hydrochloric acid with heat. The amount of silicon has, according to both methods, turned out alike. Two grammes of cast-iron, which have passed a sieve of 0·2 of a line, are shaken by small portions at a time into a beaker of 100 c.c. capacity, previously containing 18 c.c. of water with 3 c.c. pure sulphuric acid of 1·83 sp. gr., with 6 c.c. of water. The beaker is covered with a watch-glass, and placed on a water-bath; if the graphite rises on the sides of the beaker, it is pushed down into the liquid by a glass rod. When the iron is dissolved, the watch-glass is changed, after being washed, for a paper cover, and the solution evaporated on a water-bath until no condensation occurs on a watch-glass

held over the beaker; 30 c.c. of water are then added, and it is frequently stirred with a glass rod, whilst on the water-bath, until the white iron salt has completely dissolved. The insoluble mass is then thrown on a filter, and washed with hot water containing 5 per cent nitric acid, 1·2 sp. gr. (in order to dissolve all compounds of iron), as long as an iron reaction is given with ferrocyanide of potassium. The filter, with its contents, is placed in a carefully tared porcelain crucible; it is then cautiously dried, ignited, and weighed. The purity of the silica is examined by the method previously mentioned, when considered necessary. If the cast-iron contains vanadium, this is obtained for the most part as a yellow-brown vanadic acid with the silica, from which it may be extracted by warm hydrochloric acid or by ammonia.

The amount of silicon in grey charcoal pig-iron is about 2·7 per cent, and in spiegeleisen 0·8 per cent. The amount of silicon in pig from coke blast-furnaces is rarely more than 4 per cent. The least quantity of silicon in grey cast-iron is about 0·2 per cent, and in white (spiegeleisen) 0·01 per cent. The amount is usually from 1 to 2 per cent in cast-iron suitable for the Bessemer process, and in pig-iron for puddling about 0·5 per cent. The amount of silicon in iron of different degrees of hardness from the same charge of the blast-furnace ought to be pretty well judged by the fracture, after some determinations have been made by analysis.

Estimation of Phosphorus in Iron and Steel.

The importance of ascertaining the quantity of phosphorus in iron is very great; for, although the presence of a very small quantity of phosphorus in cast-iron does not produce any sensible modification in its properties, it nevertheless loses its most essential qualities when the proportion of metalloid amounts to some thousandths. Almost all the methods hitherto proposed consist in treating cast-iron with oxidising agents in such a manner as to cause the phosphorus to pass into the condition of phosphoric acid, which is estimated as a magnesian compound. M. V. Tantin, who has investigated this subject, states that several sources of error are inherent to this method, for the following reasons:—

1st. Part of the phosphorus escapes the action of the oxidising agents, and is evolved as a hydrogen compound.

2nd. It is necessary to work upon very dilute liquids, in order to avoid an admixture of oxide of iron with the ammonio-magnesian phosphate; under these conditions it is difficult to collect the small quantity of phosphate disseminated upon the sides of the vessel in which the precipitation takes place.

3rd. Any arsenic which may be contained in the cast-iron will be contained in the precipitate as an arseniate, whose insolubility is equal to that of the phosphate.

In order, therefore, to avoid these sources of error, M. Tantin concludes that the best way of so doing will be to use a precisely contrary method, namely, by liberating the phosphorus as an hydrogen compound; but one objection naturally arises—will the whole of the phosphorus pass into the state of a gaseous product? Experiment shows that there is not the least trace of phosphorus in the residue after the complete attack of the cast-iron by hydrochloric acid, which fact is not surprising if it be considered what strong affinities phosphorus has for hydrogen. The phosphide of hydrogen produced by the action of hydrochloric acid upon cast-iron is almost always accompanied by sulphuretted, arseniuretted, and carburetted hydrogen. In order to effect the separation of these gases, first pass them into a Woulff's flask containing a solution of potash, which absorbs the sulphuretted hydrogen; the other gases are then made to traverse a solution of nitrate of silver, which transforms the arseniuretted hydrogen into arsenite of silver, soluble in the slightly acid liquid, whilst the phosphuretted hydrogen precipitates the silver solution and forms an insoluble phosphide. The phosphorus being thus completely separated from the sulphur and arsenic, its estimation is effected in a simple manner. The phosphide of silver is treated with aqua regia, and thus transformed into chloride of silver and phosphoric acid, which is precipitated in the state of ammonio-magnesian phosphate. To get accurate results by this process, the following precautions are indispensable:—

1st. The cast-iron must be attacked very slowly, or part of the phosphuretted hydrogen may traverse the solution of nitrate of silver without being absorbed.

2nd. When the solution of the cast-iron is finished, a current of hydrogen, previously washed in acetate of lead, must be passed through the flask.

Mr. Tosh estimates the phosphorus in the following way. 3 grammes of the iron are dissolved in aqua regia, the solution evaporated to dryness, and the insoluble matter filtered off. The perchloride of iron solution is reduced to the state of protochloride, by heating with sulphite of soda. Although perfectly reduced, the solution still retains a yellow colour, due to dissolved organic matter. All excess of sulphurous acid is boiled off, a little perchloride of iron is added, and the solution cautiously neutralised by means of carbonate of sodium or ammonium, till the precipitate formed does not dissolve again. This small portion of peroxide of iron contains all the phosphoric acid. It is filtered off, washed, re-dissolved in a little hydrochloric acid, and the phosphoric acid precipitated as ammonio-phosphate of magnesium, the iron being held in solution in the ammoniacal liquid by citric acid.

Many skilful analysts consider that this method of throwing down the phosphorus as iron-salt and then estimating the phosphoric acid with magnesia, is unreliable, and prefer to empty the phospho-molybdate process. (See the

chapter on Phosphorus.) Other chemists, however, consider that the old plan is the preferable one. Dr. Noad says the following precautions are needed to ensure accuracy when dealing with iron and steel containing very small amounts of phosphorus. The solutions should not be too bulky. When estimating phosphorus in iron and steel, from 75 to 100 grains should be taken, and the solution, at the time of adding the tartaric (or citric) acid, ammonia, and sulphate of magnesium, must never be allowed to exceed in volume 3 fluid ounces. The first precipitate always carries down a little iron, which is removed by re-solution and re-precipitation after the addition of a fresh small quantity of tartaric acid. The first precipitate must not be collected till after the liquid has stood for twenty-four hours; the second precipitate is quite white, and may be filtered off after half an hour; it contains the whole of the phosphoric acid.

Estimation of Manganese in Iron.

The analytical separation of manganese from iron will be found under the heading Manganese, but it may save trouble if there is here given the most trustworthy methods of estimating small quantities of manganese when present in metallic iron.

After the silicon is determined in the iron or steel by Eggertz's method (p. 93), the manganese may be estimated in the same amount of material. The filtrate from the silica is diluted with water until it measures 400 c.c. and accurately divided into two portions of 200 c.c. each, one of which is set on one side, and in the other the manganese is estimated in the following manner:—(In the case of wrought-iron and steel, where 3 grammes are taken, the solution is diluted to 200 c.c., and the manganese estimated without dividing the solution). A saturated solution of carbonate of sodium is added to the solution until it becomes nearly neutralised, appearing of a deep brown colour; water containing 5 per cent of carbonate of sodium is then added, drop by drop, until a slight turbidity occurs in the solution; and if, on standing in the cold, this turbidity rather increases than diminishes, sufficient carbonate has been added (if too much carbonate of sodium has been added, and a precipitate is thrown down, the excess must be neutralised by hydrochloric acid); to the slightly turbid solution add 1½ c.c. of hydrochloric acid, and heat on the water-bath until the solution becomes clear; dilute with about half as much water as the volume of the solution, and add 30 c.c. of a saturated solution of acetate of sodium, boil for a quarter of an hour, allow the precipitated iron to settle, and decant the clear liquid through a filter, washing the iron by decantation with boiling water containing ½ per cent of acetate of sodium; finally, throw the iron on the filter, and continue the washing until bromine water gives no reaction, showing that all the manganese has passed through the filter; evaporate

the filtrate down to 400 or 500 c.c.; and at the temperature of 50° C., add a few drops of bromine to precipitate the manganese, and keep it near to that temperature for twelve hours, stirring occasionally with a glass rod; the solution after addition of the bromine becomes of a yellow or brownish colour, but should be perfectly colourless before filtering. The manganese is now thrown on a filter which has been dried at 100° C., and accurately weighed, washed with cold water containing 1 per cent of hydrochloric acid, dried at 100° C., and weighed. The precipitate is a hydrated oxide of manganese containing 59·21 per cent of manganese. The precipitate may also be ignited in a porcelain crucible at a white heat, and is then an anhydrous oxide of manganese containing 72·05 per cent of manganese.

Another method for estimating the manganese is to dissolve 3 or 4 grms. of iron in aqua regia; the solution is largely diluted and filtered, and neutralised with carbonate of sodium or ammonium till of a deep brown colour. The iron is precipitated by acetate of sodium, and the solution immediately boiled. The bulky precipitate settles quickly; the clear liquid is poured off and filtered. After three washings by subsidence and decantation, the precipitate is thrown on a large filter and again washed. The bulky solution containing all the manganese is evaporated to a small volume and re-filtered. The manganese is first precipitated by sulphide of ammonium, the sulphide collected and washed with sulphide of ammonium water, re-dissolved in hydrochloric acid, the solution boiled, and the manganese re-precipitated as carbonate by carbonate of sodium, filtered off, washed, dried, and ignited till of constant weight.

Mr. J. Spear Parker has discovered that, when copper is also present, this metal is precipitated along with the manganese; and since most specimens of spiegeleisen contain 0·2 or 0·3 per cent of copper—sometimes 0·5, or even more—the precipitation of the copper with the manganese would seriously impair the accuracy of the determination. In order to ascertain accurately how much copper the manganese would carry down when the usual process of analysis was adopted, the following experiments have been tried:—The finely-divided spiegeleisen, after solution in hydrochloric acid, was peroxidised with chlorate of potassium; the excess of chlorine was boiled off, the solution diluted, brought to boiling, neutralised with ammonia, and the iron precipitated by addition of a boiling solution of acetate of ammonium (feebly acid). After boiling for an hour, the precipitate was allowed to subside, then filtered and washed with boiling water, the residue dissolved in hydrochloric acid, and the precipitation repeated. The two filtrates were concentrated to a small bulk by evaporation. When copper is present in appreciable amount, this solution has a distinct blue tint. If necessary, the solution was again filtered, carefully washed, the filtrate heated, slight excess of ammonia added, and then bromine till the

manganese was completely precipitated. After standing for twelve or eighteen hours, the precipitate was filtered; the filtrate is always colourless. The ignited proto-sesquioxide of manganese, obtained in this manner from 20 grains of a spiegeleisen containing copper, was dissolved in hydrochloric acid; the solution, which was of a bright green colour, was diluted and transferred to a weighed platinum crucible. A piece of pure zinc was added, and the crucible was almost immediately covered with a copper-red deposit. After complete precipitation of the copper, and solution of the zinc, the liquid was decanted, and the crucible washed several times with boiling water; finally, dried in the water-bath. The copper thus obtained weighed 0·07 gr. To ascertain how much copper it was possible to precipitate with the manganese, a solution containing sulphates of copper and manganese in equal amount was precipitated with bromine, keeping the solution as nearly as possible neutral. (The precipitate is of a lighter brown when containing copper than the pure hydrate dioxide.) On igniting, it first changed to a fine black colour; after strong and protracted ignition, to brown-black. After weighing, the copper was determined as before, when it was ascertained that the two metals were present together in the proportion of nearly 1 equivalent of copper to 2 of manganese. The copper can be extracted from the moist precipitate by boiling with strong solution of ammonia, or by digestion with cold dilute sulphuric acid (in the latter case, a small portion of manganese also is dissolved). The compound seems to be somewhat unstable; for if, during precipitation, the solution be allowed to become more strongly acid, or if, on the other hand, excess of ammonia be maintained throughout, the proportion of copper is considerably diminished, especially in the latter case.

Two methods may be used to remedy this error: either to separate the copper previous to the precipitation of the manganese; or to determine the amount of copper in the ignited oxide, and then subtract an equivalent amount of oxide of copper from the total weight of the precipitate.

In using the first method, 20 grains of the finely-divided spiegeleisen are completely dissolved in hydrochloric acid, diluted, and a current of sulphuretted hydrogen passed through the liquid. After standing for twelve hours, the solution is filtered and washed with water containing sulphuretted hydrogen; the filtrate is boiled, 10 grs. of chlorate of potassium added, the iron separated, and the manganese estimated in the usual manner. If the method used be that of determining the copper in the precipitate, the estimation must be made with the greatest care, on account of the small quantity of copper present; the solution must be decanted immediately the zinc is completely dissolved, and excess of acid must be carefully avoided, otherwise the film of copper will partially re-dissolve. It is evident that, if the precipitation be effected by sulphide of ammonium

or carbonate of sodium, separation or estimation of the copper is likewise necessary.

Dr. Wolcott Gibbs proposes to precipitate manganese as ammonio-phosphate, weighing as pyrophosphate. This method gives very accurate results in pure solutions, but, in spite of every precaution, a minute amount of copper is dragged down with the precipitate in the presence of manganese; it is also liable to the objection that calcium, magnesium, &c., when present, would also be precipitated.

The accurate determination of manganese in spiegeleisen is of importance commercially; as, being the most important constituent, the value of the material is frequently judged by the percentage of that element alone, while the error introduced by the presence of copper is aggravated by the fact that, not only is copper worthless, but absolutely injurious.

Estimation of Titanium in Iron.

The detection of titanium in iron is easy, although its estimation is very difficult. Many methods have been tried in the author's laboratory, but none appear perfectly satisfactory. The best results have been obtained by following Riley's plan.* This is essentially as follows:—A weighed portion of the iron borings are treated with fuming nitric acid in a flask, a few drops of hydrochloric acid added from time to time, the whole being well boiled. The contents of the flask are then transferred into a porcelain dish, evaporated to dryness, and heated strongly. On cooling, it will be found that the oxide of iron readily detaches itself from the dish, and can be easily transferred into a beaker, the portions left on the dish being dissolved in hydrochloric acid, and poured on the contents of the beaker; the dish may be rinsed out, if necessary, with strong hydrochloric acid. The contents of the beaker are boiled for from two to three hours until complete solution of the iron is effected; and as some quantity of hydrochloric acid is required for this, the best plan is to allow a large portion of the excess of acid to evaporate in the beaker, retaining only as much as is requisite to keep up in solution the iron. The silica is filtered off in the usual way, after diluting with water and adding a few drops of hydrochloric acid on the filter, to dissolve the basic salt formed by the water. By this means the silica can be obtained nearly white after burning off the graphite, and very little iron will be found with it unless much phosphorus be present, as the silica invariably contains more or less phosphate of iron from the insoluble phoshide of iron, which cannot be completely dissolved out by hydrochloric acid. Before determining the titanium, the residue from the silica should be fused with bisulphate of potassium, dissolved in water, and added to the solution of iron in which the titanium is to be determined. The solution

* Chemical News, viii., 226, 233.

is reduced with sulphite of sodium, and the excess of sulphurous acid is driven off by boiling. The solution is then nearly neutralised with ammonia, and acetate of ammonium or sodium added; if there is only a small quantity of phosphoric acid, there will always be sufficient peroxide of iron to precipitate it, but if not, a few drops of nitric acid must be added so that the precipitate produced is distinctly red, and the solution boiled and filtered as quickly as possible. The residue is fused with bisulphate of potassium, or where nitric acid is used, this is driven off with sulphuric acid. The result of the fusion with bisulphate of potassium is dissolved in cold water (when a little phosphate of iron, which remains insoluble, is separated), boiled for some hours, and allowed to stand a night in a warm place, when the titanic acid is filtered off and washed with dilute sulphuric acid, dried, ignited, and weighed.

The above process is not very satisfactory for the quantitative determination of titanic acid. The phosphate of iron (insoluble in the bisulphate of potassium) cannot be washed without its passing through the filter, and very frequently, also, the small amount of iron keeps up the titanic acid, as iron even in small quantities has a very great effect in preventing the precipitation of titanic acid, so that it is always advisable to add a litle sulphite of sodium, which reduces the oxide of iron and facilitates the precipitation of the titanic acid.

Titanium may, however, be found more satisfactorily and more readily, during the process usually adopted to determine the amount of graphite in pig-iron, provided a large quantity of the pig be operated on. About 200 grains of the pig are to be dissolved in dilute hydrochloric acid; when the pig is nearly all dissolved, and the action of the acid has ceased, more hydrochloric acid is added, and the solution well boiled, so as thoroughly to extract all the iron. The solution is then thrown on dried counterpoised filters encircling each other, and the filter well washed to remove all the iron. It is then treated with dilute potash, and washed once; then re-treated with it so as to entirely remove the silica. The potash is thoroughly washed out, and the filter treated with hydrochloric acid, thoroughly washed and dried at 250° F. until the weight is constant. This gives the graphite, on burning which a residue of a dirty light brown colour is left, which, fused with bisulphate of potassium and subsequent treatment as above explained, is seen to be nearly pure titanic acid.

Mr. Tosh advises the approximate estimation of titanium in iron to be effected in the following way:—About 6 grammes of iron are dissolved in hydrochloric acid, and the whole evaporated to dryness. The dried mass is moistened with hydrochloric acid, water added, and the solution filtered. Part of the titanium exists in the solution (*a*) and part in the insoluble (*b*). The solution, if containing much perchloride of iron, is reduced by sulphite

of sodium, the excess of sulphurous acid boiled off, a little perchloride of iron added, and the titanic acid precipitated in combination with the sesquioxide of iron thus introduced, by means of carbonate of sodium, as in the estimation of phosphorus. The small precipitate is quickly filtered off, washed, dried, ignited, and carefully set aside. From the insoluble matter (*b*) graphite is burned off, and the silica is removed by hydrofluoric acid in the presence of sulphuric acid. To the residue after this treatment the small ferruginous precipitate from (*a*) is added, and the whole fused with bisulphate of potassium. When cool, the fused mass is extracted with cold water, and from the clear filtered solution titanic acid and iron are precipitated by ammonia; the precipitate is slightly washed, and sulphide of ammonium added. The sulphide of iron thus formed is dissolved by sulphurous acid, while the titanic acid mixed with sulphur is undissolved, and may be collected, ignited, and weighed, after which it should be tested as to its purity.

Titanium may also be estimated by loss according to the following plan devised by Riley, but this determination is not so satisfactory as a direct determination, and the results obtained are probably a little high:—About 15 or 16 grains of the iron are dissolved in nitro-hydrochloric acid, and the solution evaporated to dryness, the silica separated in the usual way, and volatilised with hydrofluoric and sulphuric acids, the residue fused with a little bisulphate of potassium, dissolved in cold water, and added to the filtrate from the silica. The solution is precipitated with acetate of sodium or ammonium, first nearly neutralising it with ammonia; after boiling well, the basic peracetate of iron is filtered off, and well washed, adding occasionally a drop or two of the alkaline acetate. The precipitate is then dissolved in hydrochloric acid, and the peroxide of iron precipitated by ammonia, filtered, dried, and ignited in the usual way. The peroxide of iron is then dissolved in hydrochloric acid, and, the small amount of silica present separated, the solution is reduced with sulphite of sodium, and the iron determined with a standard solution of bichromate of potassium. This will give the percentage of pure peroxide of iron; and the difference between the peroxide of iron weighed and that determined by standard solution is considered to be titanic acid and phosphoric acid. The phosphoric acid having been determined by another distinct operation, the amount present in the peroxide of iron is calculated and deducted from the above difference—the remainder being considered to be titanic acid, from which the percentage of titanium in the iron is calculated.

In testing a siliceous residue for titanic acid with hydrofluoric acid it must be remembered that a fluoride of titanium is formed at the same time, which cannot be heated without the larger portion going off. Riley*

* Journ. Chem. Soc., xii., 13.

describes an experiment in which 2·235 grms. of titanic acid exposed (with the occasional addition of water) for 24 hours to the action of hydrofluoric acid in Brunner's apparatus, until it was completely dissolved, left, on evaporating to dryness and heating carefully to a low red heat, a residue of only 0·99 grm., which still contained a trace of fluorine. Hence it follows that residues obtained by this method only represent a portion of the titanic acid actually present.

In estimating the amount of titanium or titanic acid in samples of cast- or wrought-iron, this substance has usually been sought for in the residue insoluble in acids, but, according to the following experiments of Mr. Forbes, such a procedure cannot be relied upon as furnishing correct results.

A sample of cast-iron produced from smelting a titaniferous magnetite from Gullaxrud, in Norway, in a charcoal blast-furnace, was taken, and 251·59 grains in small fragments dissolved in nitro-hydrochloric acid; the insoluble residue was collected on a filter, incinerated, digested with sulphuric acid, and the titanic acid present determined as described at p. 111, when it was found to amount to 0·52 grain, equivalent to 0·207 per cent titanic acid, or 0·126 per cent titanium.

The filtrate was now neutralised carefully with ammonia, and then a slight excess of ammonia added, so as to cause a small permanent precipitate of sesquioxide of iron to be formed, which was then filtered off from the ferruginous solution, and washed. This precipitate, which contained all the titanic and phosphoric acid present in the iron, along with an excess of sesquioxide of iron, was now dissolved in a little very dilute sulphuric acid, some nitric acid added, and the solution boiled; an immediate precipitate of titanic acid was formed, which, when determined, amounted to 0·14 grain, or 0·056 per cent, equivalent to 0·034 per cent titanium. The examination of this cast-iron resulted in showing that it contained 0·207 per cent titanic acid in the insoluble form, and 0·056 per cent titanic acid in the soluble form, or a total of 0·623 per cent titanic acid, and that, consequently, more than 20 per cent of the entire titanic acid had been dissolved by the acids employed in the analysis.

Another sample of cast-iron was also examined with the same object in view. In this case 104·26 grains of the cast-iron in fragments were dissolved in nitro-hydrochloric acid, and left an insoluble residue which, after incineration, weighed 2·47 grains; this was, as in the last case, digested in concentrated sulphuric acid; the titanic acid, which was determined as before described, weighed only 0·02 grain. The acid filtrate was then treated with ammonia, so as to precipitate a small amount of the sesquioxide of iron along with any titanic acid contained in the iron, and this latter determined as in the former case, amounted to 0·03 grain.

The result of this experiment shows, therefore, that this cast-iron contained a total of only 0·048 per cent titanic acid, of which 0·019 per cent remained in the insoluble residue, whilst 0·029 per cent had been dissolved in the acid solution, confirming the previously arrived at conclusion, that when a very small amount of titanic acid is present in a substance, the major part of it is often, if not always, to be found in the solution, and not in the insoluble residue.

For special methods for the detection of sulphur, phosphorus, silicon, titanium, &c., see the chapters treating on these elements, and on Silicates.

EXAMPLES OF THE ANALYSIS OF IRON, STEEL, AND IRON ORES.

In the preceding pages we have given methods for the detection and estimation of the carbon, sulphur, phosphorus, and other elements associated with commercial iron and steel. When these are required to be estimated in the same specimen of metal or ore, some of the methods can be materially shortened, as will be seen by the following examples of methods for the complete analysis of iron, steel, and iron ores which have been selected in illustration.

Analysis of Blister Steel.

Mr. David Forbes, gives the following particulars* of the analysis of blister steel converted in Sheffield from bar iron of Swedish manufacture. The portion selected for examination was obtained in a sufficiently divided state by chipping off the bar with a cold chisel, since it was found that no reliance could be placed in filings, which even if produced by the best files were always contaminated by the *débris* of the file itself; the determination of the constituents was made as follows:—

Determination of the Total Amount of Carbon.—77·91 grains of the steel, in the form of such chippings, were allowed to remain for about ten days in a cold solution of 200 grains of pure chloride of copper, until no undissolved steel remained behind; the residue was then well washed by decantation, dried, mixed with 100 grains of pure oxide of copper, and burnt in a current of purified dry oxygen gas, at a heat sufficient to soften the Bohemian glass tube. The carbonic acid collected as usual in a potash apparatus, amounted to 2·08 grains, or equivalent to 0·729 per cent of carbon in the steel.

Determination of the Sulphur.—107·58 grains were placed in a flask provided with a safety-funnel, and digested for twenty-four hours in the cold, with strong hydrochloric acid; the gas evolved was passed through a

* Chemical News, xvi., 105.

solution of pure chloride of zinc supersaturated with ammonia; the iron being all dissolved, the zinc solution was boiled with nitric acid in some excess, nearly neutralised by ammonia to prevent any solvent action from excess of acid, and precipitated by a solution of pure chloride of barium—0·04 grain sulphate of barium was obtained, equivalent to 0·005 per cent sulphur in the steel.

Determination of the Silicon and Uncombined Carbon.—The solution from the above was evaporated in a water-bath to dryness, re-dissolved in water with some hydrochloric acid, and filtered from the insoluble silica and graphite; these latter were washed off the filter into a silver basin, in which they were boiled with potash, which dissolved out the silica, leaving the graphite, which was collected on a filter, washed, dried, carefully scraped off the filter, and dried at 250° F.; it weighed 0·11 grain, equivalent to 0·102 per cent uncombined or graphitic carbon. The potash solution of silica was supersaturated with hydrochloric acid, evaporated to dryness, and the residue treated with water rendered acid by hydrochloric acid. The silica was then filtered off and determined as usual, being 0·06 grain, or equivalent to 0·0304 per cent silicon in the steel.

Determination of the Manganese.—The acid filtrate, after separating the graphite and silica by filtration, was now nearly neutralised by ammonia, and then treated with carbonate of barium in excess, filtered, and the filtrate precipitated by sulphide of ammonium. The sulphide of manganese mixed with some sulphate of barium was then treated with weak sulphuric acid, filtered, and the manganese precipitated by carbonate of sodium, affording 0·18 grain manganoso-manganic oxide, or equivalent to 0·12 per cent manganese in the steel.

Search for Phosphorus.—52·75 grains of the steel treated precisely according to Abel's directions,* afforded no trace of ammonio-phosphate of magnesium. 73·28 grains examined by Spiller's process* gave the same negative result; and, lastly, 48·07 grains tested by Eggertz's method by molybdate of ammonium* did not afford any trace of phosphorus.

Determination of Iron.—The amount of iron present was estimated as loss. The percentage results were as follows:—

Carbon combined	0·627
,, graphitic	0·102
Silicon	0·030
Phosphorus	—
Sulphur	0·005
Manganese	0·120
Iron	99·116
	100·000

* See chapter on Phosphorus.

Analysis of Magnetic Iron Ore.*

The iron ore here under consideration was strongly attracted by the magnet, and, with the exception of traces of iron pyrites and pyrrhotine, all the iron was present in the state of magnetic oxide (magnetite). The percentage of metallic iron, besides being calculated from the amount of sesquioxide of iron obtained in the course of the analysis, was also determined in a separate portion of the ore by the bichromate of potash volumetric process, after its previous solution and reduction to the state of protoxide, by metallic zinc: the oxygen combined with the iron was estimated from the loss in analysis. The portion of the mineral employed for determining the amount of sulphur was dissolved in nitro-hydrochloric acid, filtered from the insoluble siliceous matter, and the filtrate evaporated nearly to dryness in a water-bath, so as to expel the excess of free acid (which otherwise might augment the solubility of the sulphate of barium), and after having been precipitated by chloride of barium, the sulphate of barium was estimated as usual. Phosphorus was sought for in a larger amount of the ore, both by Abel's and Spiller's processes, and also by the molybdate process. The manganese was separated from the iron by carbonate of barium, and the other constituents, carbonic acid, calcium, magnesium, and aluminium, determined as usual.

Analysis of Spathic Iron Ore.

Professor Wöhler gives the following process for the analysis of spathic iron ore :—Dissolve a weighed quantity of the finely ground ore in hydrochloric acid, to which is added a little nitric acid or chlorate of potassium. Precipitate with ammonia, but be careful not to filter until the liquid had been boiled till all odour of ammonia has disappeared; the iron precipitate then contains no trace of calcium, magnesium, or manganese. The liquid containing no trace of free ammonia, the filtration may be performed in contact with air. The filtrate must be concentrated by evaporation, and the three bases which it contains precipitated with an excess of carbonate of potassium, continuing the ebullition so long as no ammonia is disengaged. Filter the liquid and re-dissolve the precipitate in nitric acid, then evaporate to dryness, and carefully heat to dull redness. Dilute nitric acid will then separate the lime and magnesia from the insoluble oxide of manganese.

Analysis of Titaniferous Iron Ore.

The composition and metallurgy of titaniferous iron ores (Norwegian) have received great attention from Mr. David Forbes, whose experience in this subject dates from 1847. He gives the following process for analysing

* By Mr. Forbes (Chemical News, xvi., 259).

them:*—A weighed amount of the ore is fused in a gold crucible with eight times its weight of bisulphate of sodium, until all soluble matter has been taken up. The fused mass is treated with cold water until nothing remains but some pure white silica, which is filtered off, washed, and determined; to the solution, much diluted with water, a few drops of nitric acid are added (in order to prevent the titanic acid carrying down sesquioxide of iron along with it), and the whole boiled for a considerable period. The titanic acid thus precipitated is determined after ignition, when it possesses a light yellow colour. The aluminium, iron, calcium, and magnesium in the filtrate are now separated as usual, and the determination of the iron checked by the volumetric process (by bichromate of potassium) upon a separate portion of the ore dissolved in nitro-hydrochloric acid, and also used for determining the amount of sulphur present. If phosphorus is present, it is separated by fusion with carbonate of sodium, and afterwards determined as pyrophosphate of magnesium in the usual manner.

Immediate Analysis of Meteoric Iron.

The numerous researches hitherto made with regard to the composition of meteoric irons, have demonstrated the existence of the following compounds in these extra-terrestrial bodies:—

1. The *general mass*, which is formed by the union of several alloys in which iron and nickel are predominant, and which we will designate under the name of *nickeliferous iron*. Among the substances comprised in this mass, *kamacite*, *tænite*, and *plessite* are specially noticeable.

2. The *carburetted iron*, comprising *campbellite* and *chalypite*, recognisable by the carboniferous deposit which they give under the action of acids.

3 *Sulphuretted iron*, or *troilite*, which appears in nodules and in veins.

4. *Phosphide of iron and nickel*, or *Schreibersite*.

5. *Graphite*.

6. *External crust*.

7. *Stony particles*, or *crystals*.

8. *Gases* retained by occlusion.

9. Several compounds which are only met with exceptionally, as *chromite* and *protochloride of iron*.

(The last may indeed have a terrestrial origin, according to the opinion of Mr. Shepard.)

M. Stanislas Meunier, Aide Naturaliste at the Museum of Paris, has tried to separate these different substances, and has submitted each of them to a special examination. His experiments, which have resulted in

* See chapter on Phosphorus.

the fixation of their chemical formulæ, were communicated to the "Chemical News" for January, 1869, and are given in abstract in the following pages.

I. **Nickeliferous Iron.**—The first problem to be solved is the separation of the different alloys which are mixed in the general mass of meteoric irons; but it is necessary first of all to prepare that general mass free from other substances already named. For this end, the iron being reduced to powder by means of a hard file, the metal is thrown into pure potash, in a state of fusion, in a silver crucible. Instantaneously the alkali, hitherto limpid, becomes turbid, owing to the presence of little grey flakes, which consist of oxide of iron and are the result of decomposition of troilite, schreibersite, stony matters, &c.

When this decomposition of foreign substances is complete, the alkaline mass is cooled and treated by water. All the potash is washed away with the greater part of oxide of iron. The remainder of this oxide is easily dissolved by strong nitric acid, in which the metallic iron becomes passive. The metallic powder is then well washed and dried; it is formed exclusively of nickeliferous iron, containing, however, in certain cases, a small proportion of carburetted iron.

Chemical methods have not yet completely succeeded in separating the alloys mixed in the nickeliferous iron, and, after several essays, M. Meunier was obliged to have recourse to physical processes. His experiments have been made with the meteoric irons of Caille (France), and of Charcas (Mexico).

It was necessary, first of all, to determine with accuracy the number of constituent compounds contained in the nickeliferous iron of these masses. For this purpose a small polished plate of the iron of Caille was carefully and uniformly heated. This operation, of which the first idea is due to Widmanstætten, drew, by the unequal oxidation of the different immediate principles, a yellow net upon a blue ground. There were also several portions of an intermediate colour, clearly limited like the others, and occupying the spaces bounded by the crossing of the yellow lines. An attentive examination showed that the three metallic compounds were reducible to two; the third being formed by the mixture of the others, reduced to alternate thin sheets. The blue colouration is formed by kamacite, and the yellow by tænite.

Their separation was very difficult, on account of the analogy of the chemical properties of the two metals. Although it is true that kamacite is more soluble than tænite (and this is proved by the experiment of Widmanstætten), this difference is too small to permit of a separation. When all the kamacite is dissolved, only a very small proportion of tænite remains, the greatest part being dissolved also.

To effect the separation, some metallic powder was heated upon a glass plate. The particles formed by kamacite became blue, whilst the particles of tænite were yellow. The two sorts of grains were then separated with pincers. After about fifteen operations, 2 grms. of kamacite, and 0·5 grm. of tænite, were collected fit for chemical examination. The Charcas iron gave the same results.

The specific gravity of tænite is 7·380. Its analysis yielded the following numbers:—

Iron	85·0
Nickel	14·0
	99·0

which agree with the formula Fe_6Ni.

Kamacite has a specific gravity of 7·652, and its composition was found to be—

Iron	91·9
Nickel	7·0
	98·9

Agreeing with the formula $Fe_{14}Ni$.

On this subject it will be remarked that, admitting, according to the numbers given above, that the Caille iron contains 80 per cent of kamacite and 20 per cent of tænite, its elementary formula will be expressed by

$$Fe_6Ni + 4(Fe_{14}Ni) = Fe_{62}Ni_5,$$

which gives numbers very near those which M. Rivot obtained in the elementary analysis of that mass.

The above formula gives—

Iron	91·4
Nickel	8·6
	100·0

Whilst M. Rivot found, in two analyses—

Iron	92·3	92·7
Nickel	6·3	5·6
	98·6	98·3

All meteoric irons are not so simple as those of Caille and of Charcas. There are some which contain, with kamacite and tænite, a certain quantity of other metallic alloys. One of the most important of these is plessite, which abounds, for example, in irons of Jewell Hill (North Carolina), and of Oldham (Kentucky). This has been isolated by the same method which served for the preceding substances. Plessite has a density of 7·850, and its composition appears to be satisfactorily represented by the formula $Fe_{10}Ni$.

Amongst the other alloys of iron and nickel may be mentioned *octibbehite*, whose composition is exceedingly remarkable, owing to the large proportion of nickel (59·60 per cent) it contains. Its density is only equal to 6·854. The meteoric iron of Octibbeha (Mississipi) seems to be entirely formed of that alloy, according to the researches of Mr. Taylor.

II. **Carburetted Iron.**—Several meteoric irons give, by the action of acid, a black deposit, more or less abundant, consisting of carbon. This carbon comes from a compound whose position is analogous to that of steel. In this point of view, the meteoric iron of Campbell (Tenessee) may be specially mentioned. It gives, on analysis, a metallic substance, formed by the union of 1·50 per cent of carbon with 97·54 per cent of iron. For it the name of *campbellite* may be proposed; its density is 7·05. Mr. Shepard gives the name of *chalypite* to a carbide of iron which Forchhammer has detected in the meteoric iron of Niakornak (Greeenland), and of which the formula is CFe_2.

III. **Sulphuretted Iron.**—To prepare the sulphuretted iron, or *troilite*, in a complete state of purity, we may have recourse to the metallic powder. This powder is placed for a quarter of an hour in a boiling concentrated solution of sulphate of copper. All the nickeliferous iron is dissolved, and, by decanting and washing, a mixture of metallic copper, troilite, schreibersite, graphite, and stony matter may be obtained.

A small quantity of concentrated nitric acid dissolves the copper. The magnet, acting under water, is the best means to separate troilite and schreibersite (which are magnetic) from graphite and stony matter. Finally, lixiviation can be employed to separate troilite from schreibersite.

When the iron under experiment contains only a small quantity of troilite, it is preferable not to use nitric acid, which always dissolves a little of the desired substance. In such cases the nickeliferous iron may be dissolved by means of bichloride of mercury. The protochloride of mercury is carried off by a solution of chlorine, and it is easy to separate the metallic mercury.

It is, however, always better, when possible, not to extract troilite from the iron, but from the cylindroid nodules in which the substance has concentrated. In these the sulphuretted iron contains only some graphite and stony matter, which can be got rid of by the action of the magnet. There is no doubt that this troilite is one of the most characteristic principles of meteoric iron. Notwithstanding which, its crystalline form has not yet been recognised, and there is some doubt about its chemical composition. The first chemists who examined it considered it as a variety of Breithaupt's pyrrhotine, and gave to it the formula Fe_7S_8. But Professor Lawrence Smith concluded from his estimations of the sulphur in the iron of Tazewell, that it had the composition of a protosulphide FeS. Notwithstanding

which, he continued to give it the name of pyrrhotine, and thus a great confusion was introduced into science. Moreover, Professor Smith rested both upon the results of his own experiments and upon those obtained by several chemists in the examination of other samples of troilite; his conclusion was not admitted, and the existence of true crystalline magnetic pyrites in meteorites will increase the difficulties. The distinction between the troilite (or Professor Smith's pyrrhotine) and Breithaupt's pyrrhotine, is not so clear as would appear at first sight. The difference of composition is very slight, and the physical properties are very similar.

M. Meunier has lately had occasion to analyse several specimens of troilite taken from the meteoric irons of Charcas and of Toluca (Mexico), and the numbers which he has obtained have given him reason to think that the mineral in question is nearer to magnetic pyrites than to protosulphide of iron.

Before giving the results of these analyses, we may call attention to a reaction which seems calculated to permit in all cases of the distinguishing of the protosulphide of iron from magnetic pyrites, and, *à fortiori*, from compounds which are still richer in sulphur. When protosulphide of iron is placed in a solution of copper, it precipitates this metal almost like iron itself; pyrrhotine, on the contrary, produces no such precipitation. The protosulphide obtained by the action of sulphide of ammonium upon iron salts produces the same effect as the sulphide of exactly the same composition prepared by igneous means. This being well established, several samples of troilite were put into a solution of copper, and no precipitation could be observed; troilite, therefore, is very like magnetic pyrites in this respect, and we may draw the same conclusion as to its chemical composition. In fact, Professor Smith has based the formula FeS upon his analysis of Tazewell's troilite, which gave him :—

Iron	62·38
Nickel	0·62
Copper	trace
Lime	0·08
Silica	0·56
Sulphur	35·67
	99·31

But these numbers show that the substance employed in his experiments was very impure.

Troilite purified by the process described above yielded a substance of which the specific gravity was 4·799. Its colour was bronze, and its analysis gave :—

Iron	59·01
Nickel	0·14
Copper	trace
Sulphur	40·03
	99·18

The formula Fe_7S_8 requires—

Iron	60·4
Sulphur	39·6
	100·0

The Charcas troilite, previously purified, yielded—

Iron	56·29
Nickel	3·10
Sulphur	39·21
	98·60

Its density is 4·78. The normal presence of nickel makes troilite a species distinct from pyrrhotine, and its true formula becomes $(Fe.Ni)_7S_8$.

IV. **Schreibersite.**—Schreibersite, or phosphide of iron and nickel, may be prepared by the same method as troilite. It is, besides, always preferable to select the schreibersite in the places where it is naturally concentrated. It is a yellowish, or almost white, metallic looking substance. Its specific gravity is 7·103, and contains—

Iron	57·11
Nickel	28·35
Cobalt	trace
Magnesium	trace
Phosphorus	15·01
	100·47

numbers which lead to the formula Fe_4Ni_2P. Schreibersite is magnetic, and takes permanent polarity by contact with a magnet. It is brittle. Hydrochloric acid has no action upon it. Its crystalline form has not yet been observed.

V. **Graphite.**—Graphite may be isolated by the following method:— A few grammes of metallic powder are projected into fused potash, and thus a mixture of nickeliferous iron and graphite is obtained. This mixture may be treated in several ways.

1st. The iron is dissolved in chlorhydric acid, which leaves the almost pure graphite as residue.

2nd. The graphite is separated by lixiviation. This process presents the advantage of giving both graphite and nickeliferous iron; but the separation is never complete.

3rd. When the graphite is abundant the magnet may be employed; in other cases it is drawn up with the metal.

In all cases the residue is washed by hydrochloric acid to dissolve foreign matters, such as troilite and schreibersite, or what is left from their attack by fused alkali.

The graphite extracted from the Caille iron has a specific gravity of 1·715. Its analysis gave—

Carbon	97·3
Iron	2·4
Nickel	trace
	99·7

The graphite of the Charcas iron has a density of 1·309, and yielded on analysis—

Carbon	98·0
Iron	0·9
	98·9

The graphite is remarkable on account of its great unalterability.

VI. **External Crust.**—Those portions of meteoric iron, upon which is a crust, being separated by means of a saw, they are placed in a concentrated solution of bichloride of mercury. After a sufficient time all metallic particles are dissolved, and the oxides, amongst which is the crust, remain alone.

The crust is, however, still mixed with foreign matters. It usually contains with it the products of its alteration by atmospheric agents, and particularly limonite. Some schreibersite, troilite, and stony grains may also be mixed with the principal substance, and their separation is very difficult. Weak hydrochloric acid carries away limonite and troilite; earthy particles remain as residue after the action of the magnet; lixiviation permits of the purification of the crust from schreibersite. These operations may, however, be simplified by choosing those portions of the crust that seem almost pure. They frequently detach themselves from the subjacent metallic matter.

Very few chemists have analysed the external crust of meteoric irons. The analyses given by Pugh, as showing the composition of the crust of the Toluca iron, were evidently executed on an impure portion. These are Pugh's results:—

Metallic iron	18·717
Protoxide of iron	19·309
Sesquioxide of iron	32·750
Protoxide of nickel and of cobalt	5·751
Chalk	trace
Silicates	10·203
Water	13·270
Chlorine	trace
	100·000

The metallic iron, silicates, and water are evidently not essential elements of the crust, and must be considered as impurities.

Having purified as much as possible by the method above described the crust of the Toluca meteoric iron, M. Meunier found it possessed a density of 4·89, and the following composition:—

Sesquioxide of iron	68·93
Protoxide of iron	28·12
Protoxide of nickel	2·00
Protoxide of cobalt	trace
	99·05

These numbers agree with the formula $Fe_2O_3,(FeNi)O$, which does not differ from that of magnetite, except by the substitution of a small portion of nickel for a corresponding quantity of the iron of the protoxide. If in Pugh's analysis we only consider sesquioxide of iron, protoxide of iron, and protoxide of nickel and of cobalt, we arrive at numbers very near to those required by the above formula.

VII. **Stony Grains.**—Several of the operations described above evidently yield the stony grains in a state of purity. But when it is especially intended to obtain these grains, they should be separated in the following way:—

The meteoric iron in the form of lumps is left protected from the contact of the air in a concentrated solution of bichloride of mercury, and frequently stirred. After a sufficient time, the metal disappears, and the liquid contains the stony particles mixed with protochloride of mercury, and generally with a small quantity of metallic mercury, besides troilite, schreibersite, and graphite. A solution of chlorine carries off the calomel, and the magnet removes the schreibersite and the troilite; lixiviation may be employed to get rid of graphite.

These grains are of different composition, and it appears that there exists a certain relation between their composition and their situation. Some are localised in the iron; others are situated in the troilite, or, perhaps, in the graphite which surrounds this sulphide.

The grains of the first category may be found in meteoric irons of Tazewell and of Tuczon. They consist of peridote, and this is confirmed by the analyses published by Mr. Lawrence Smith. Their density is equal to 3·35.

The grains of the second category are yielded by the troilite of the Caille iron. Submitted to blowpipe assay, they only exhibit the reaction of silica.

The troilite of Charcas iron gave analogous results.

VIII. **Gases.**—Gases have been recognised in the meteoric iron of Lenarto, by Mr. Graham and by M. Boussingault.

M. Meunier has sought for the same bodies in another iron of the same

origin by effecting the solution of those masses in concentrated bichloride of mercury. As, however, he was not aware that the occluded hydrogen would be all absorbed by the solution of bichloride of mercury, reducing it to the state of calomel or metal, he erroneously considered that the absence of visible gas proved that there was no gas occluded. The mass of Krasnojarsk (Siberia) gave a small bubble of gas, having the composition of atmospheric air; but it must be remarked that this iron was cracked.

IX. **Rare Substances.**—In concluding this enumeration, chromite and protochloride of iron must be mentioned as having been found in certain irons. Their separation is evidently easy, and their composition is identical with that of analogous terrestrial compounds.

After having described the methods which have permitted him to separate in a state of complete purity the *immediate principles* of meteoric irons, M. Meunier remarks that these methods can be employed to estimate the relative quantity of the substances in question.

He has, for instance, submitted to a *quantitative immediate analysis* the meteoric iron discovered in 1784, at Xiquipilco, in the valley of Toluca (Mexico), and has found in it—

Nickeliferous iron	96·301
Graphite	1·176
Troilite	1·482
Schreibersite	1·232
	100·191

Special Methods for the Analysis of Iron Ores.*

Three principal methods of analysis may be employed, which, in the subsequent descriptions, will be denoted as Method No. I., Method No. II., or Method No. III., according as one or other was employed in the particular analysis.

Details of Method No. I.—1. A portion weighed from the stoppered bottle containing the fine powder was digested in strong hydrochloric acid till no further action seemed to take place, and was boiled for about 15 minutes before dilution and filtration. The undissolved portion was thoroughly washed with hot distilled water, dried, ignited, and weighed, the usual precautions being taken to prevent absorption of moisture.

2. The iron in the filtrate was peroxidised, if necessary, by nitric acid or chlorate of potassium; excess of ammonia was added, and filtration conducted rapidly.

* These methods were, after numerous experiments, finally adopted by Messrs. A. Dick and J. Spiller, in the analyses of the iron ores of Great Britain. ("Memoirs of the Geological Survey of Great Britain." The Iron Ores of Great Britain. Part 1: The Iron Ores of the North and North-Midland Counties of England.)

3. The calcium was precipitated from the filtrate as oxalate, converted into carbonate by ignition, and either weighed as such after evaporation with carbonate of ammonium, or else moistened with sulphuric acid, and, after expulsion of the excess of acid by heat, weighed as sulphate.

4. The magnesium was precipitated by phosphate of sodium and excess of ammonia. Generally, about 24 hours were allowed for the separation of the precipitate; it was then collected on a filter, washed with ammonia water, dried, ignited, moistened with a few drops of nitric acid, re-ignited, and weighed. The precipitate obtained by this method generally contains some flocculent matter, which was found to be phosphate of aluminium; the alumina having been retained in solution by the ammonia (2).

5. The precipitate (2), consisting of all the iron, aluminium, phosphoric acid, and manganese (except a trace of the last which accompanies the lime), together with small portions of silica and lime or magnesia—the former combined apparently with alumina, the latter with a portion of the phosphoric acid—was dissolved in hydrochloric acid, then supersaturated with caustic potash, boiled in a platinum basin, and filtered. The filtrate was acidified with hydrochloric acid, boiled, after addition of some chlorate of potassium, to destroy the organic matter arising from the action of the potash on the filter, nearly neutralised with ammonia, and finally rendered alkaline with carbonate of ammonium. The precipitate was ignited and weighed; the phosphoric acid contained in it was determined by the tartaric acid process (see par. 13), and subtracted from the previous weight to ascertain that of the alumina. The amount of phosphoric acid so determined is never exactly the correct one, owing chiefly to its containing a little silicate of aluminium. The phosphoric acid was always determined by another experiment.

6. The precipitate produced by caustic potash was dissolved in hydrochloric acid, and the iron precipitated as succinate, collected on a filter, redissolved and re-precipitated by ammonia, ignited, and weighed. So obtained, it is never perfectly pure, owing to its containing a little phosphoric acid, combined apparently with calcium or magnesium, and silica combined apparently with aluminium; neither of these combinations being decomposed by boiling with caustic potash. It was accordingly re-dissolved in hydrochloric acid, and filtered from a portion of the silica which becomes insoluble at this stage, and which was ignited and weighed. It may be here noted that a very small quantity of silica cannot be separated from a very large quantity of iron by the ordinary evaporation process; so that the separation of this small quantity of silica could not be effected by evaporation of the original hydrochloric acid solution. The phosphoric acid contained in the precipitate was determined by the tartaric acid process; so obtained, it generally contains a small quantity of silicate of aluminium.

This phosphoric acid and silica subtracted from the original weight gave what was taken as peroxide of iron; though it no doubt still contained a very small quantity of other substances.

7. The filtrate from the succinate of iron was rendered alkaline by ammonia; a few drops of bromine were added, and it was left 24 hours. The precipitate was ignited at a bright red heat and weighed as manganoso-manganic oxide.

8. The insoluble portion (1) was fused with excess of the alkaline mixture obtained by decomposing Rochelle salt by heat, and washing out the mixed carbonates. The fused mass was dissolved in dilute hydrochloric acid, evaporated to dryness, the residue moistened with strong hydrochloric acid, and left 24 hours; it was then digested with hot water, filtered, and the silica ignited and weighed. Its purity was tested by dividing it into two portions, and treating one by hydrofluoric acid and the other by caustic potash; any impurity was separated if the amount was weighable.

9. The filtrate (8) was rendered alkaline by ammonia, and filtered. The precipitate was either ignited and weighed, the iron being afterwards separated and subtracted from the previous weight, or else it was at once dissolved in hydrochloric acid, and subjected to the potash treatment described in (5) and (6), except that, since it contained no phosphoric acid, this part of the treatment was not needed.

10. The calcium and magnesium in the filtrate (9) were determined in precisely the same manner as in the hydrochloric acid solution of the ore.

11. *Alkalies and Organic Matter.*—It was ascertained that nearly the whole of the alkalies was contained in the residue insoluble in hydrochloric acid. A weighed portion of the ore was digested in hydrochloric acid, the insoluble residue collected on a filter, and washed. The latter was then dried, till, by a little management, it could be collected together and removed from the filter without detaching a weighable amount of the fibre of the paper. It was then exposed in a platinum vessel to the vapour of hydrofluoric acid in Brunner's apparatus till decomposed. The product was evaporated with strong hydrochloric acid, the residue moistened with dilute hydrochloric acid, and the undissolved black matter collected on a small weighed filter, dried, and weighed. As it generally contained a small amount of undecomposed inorganic matter, it was ignited and the ash weighed and subtracted. The filtrate from the organic matter was added to the original hydrochloric acid solution; the mixed solution was treated by the ordinary caustic baryta process for alkalies, which were weighed as chlorides.

12. *Sulphuric Acid and Sulphur.*—A weighed portion of the ore was digested in hydrochloric acid, the solution filtered, and the sulphuric acid precipitated from the filtrate as sulphate of barium, ignited, and weighed.

The residue was detached from the filter, mixed with carbonate and nitrate of potassium, and fused in a gold crucible. The fused mass was dissolved in hydrochloric acid, evaporated to dryness, moistened with strong acid, diluted, and filtered. From the filtrate the sulphuric acid was precipitated as sulphate of barium, and from this the sulphur was calculated. It seems always to have occurred as iron pyrites in the ore. In tabulating the results accordingly, the iron required to combine with this sulphur was subtracted from the percentage of insoluble residue, as well as from the composition of that residue. It may be here noted that when finely divided iron pyrites is boiled with strong hydrochloric acid and perchloride of iron, some of the latter is reduced and some sulphuric acid formed. It is important to remember this in the analysis of hæmatites.

13. *Phosphoric Acid.*—A weighed portion of the ore was digested in hydrochloric acid, and the solution filtered. The filtrate was heated (the iron reduced by sulphite of sodium when necessary), nearly neutralised with carbonate of sodium, and excess of acetate of sodium added. The liquid was boiled, and perchloride of iron added, drop by drop, to the hot solution, till the precipitate had a decidedly red colour. The precipitate was collected on a filter, washed with hot water, dissolved in hydrochloric acid, tartaric acid added, and, finally, excess of ammonia. The phosphoric acid was precipitated by addition of the mixture of sulphate of magnesium, chloride of ammonium and free ammonia, 24 hours being allowed for the precipitate to separate. It was then collected on a filter, dissolved in hydrochloric acid, and some tartaric acid added to the solution. The phosphate was re-precipitated by ammonia, collected on a filter, ignited, moistened with a few drops of nitric acid, re-ignited, and weighed.

14. *Water.*—A portion of the ore was weighed out, dried in the water-oven, and re-weighed to determine hygroscopic water. It was transferred to a tube closed at one end; the other end was then connected by a cork to a small weighed tube containing chloride of calcium. Heat was applied to the tube containing the powder, and gradually increased to low redness. The majority of the ores suffer decomposition during this, with evolution of a gas arising from the decomposition of carbonates, which prevents, in most cases, the necessity of drawing any air through the apparatus. The tube containing chloride of calcium was then re-weighed to ascertain the amount of chemically combined water. In clay ironstones this is combined with the silicate of aluminium or clay which they contain in admixture.

15. *Carbonic Acid.*—The single flask apparatus was used; sulphuric acid was employed to decompose the carbonates in the ore.

16. *Metals Precipitable by Sulphuretted Hydrogen from the Hydrochloric Acid Solution.*—A weighed portion of the ore, varying from 200 or 300 grs. to 2000 grs. was digested for a long time in hydrochloric acid. The solution

was filtered off (the iron in the filtrate reduced, when necessary, by sulphite of sodium), and a current of sulphuretted hydrogen passed through it. A small quantity of sulphur which always separated was collected on a filter and thoroughly washed. It was incinerated at as low a temperature as possible. The residue was mixed with carbonate of sodium, and heated upon charcoal before the blowpipe; and any globules of metal obtained were dissolved and tested.

Sometimes the portion insoluble in hydrochloric acid was re-digested in hydrochloric acid, and chlorate of potassium added from time to time. The solution was then filtered off, and added to the original solution before reduction of per-salts of iron.

Details of Method No. II.—A weighed portion of the ore was digested in hydrochloric acid, and the liquid filtered. The insoluble matter was fused as in Method No. I., dissolved in hydrochloric acid, and added to the original solution. The mixture was then evaporated to dryness to obtain the silica. In other respects the method of analysis was precisely similar to that described as No. I., avoiding only that part referring to the separate treatment of the matter insoluble in hydrochloric acid.

Details of Method No. III.—1. This method, owing to its greater simplicity and accuracy, was the one ultimately adopted. A weighed portion of the ore was digested in hydrochloric acid, and the liquid filtered. The insoluble matter was ignited, weighed, and treated in a manner precisely similar to that described under Method No. I.

2. The iron in the hydrochloric acid solution was peroxidised when necessary. The solution was heated, nearly neutralised with ammonia, then boiled with excess of acetate of ammonium, and filtered whilst hot. The precipitate was washed with hot water. The filtrate was received in a flask, and rendered alkaline by ammonia; a few drops of bromine were added, and the flask was tightly corked to exclude air, and left 24 hours. The liquid was then heated, and rapidly filtered; the precipitate was ignited, and weighed as manganoso-manganic oxide. The calcium and magnesium contained in the filtrate were determined as in Method No. I. It may be here noted that the ammonio-phosphate of magnesium obtained by this process is never mixed with any phosphate of aluminium, owing to the aluminium being completely precipitated as basic acetate.

3. The precipitated basic acetates (2) were dissolved in hydrochloric acid. The solution was supersaturated with caustic potash, boiled in a platinum basin, and filtered. The aluminium containing some phosphoric acid was precipitated from the filtrate as in Method No. I. The phosphoric acid was separated by the tartaric acid process; the ammonio-phosphate of magnesium was always re-dissolved and re-precipitated, but still was seldom quite pure, containing generally a little silicate of aluminium.

Another determination was always made. It was ascertained that when this method was employed no phosphoric acid remained with the iron after treatment with potash. A little silica, however, did remain, but the quantity was small, and as nothing further was done with the iron after treatment with potash, this was lost from the analysis, a more accurate method for the determination of the iron being employed.

4. *Iron.*—Two determinations were always made by Dr. Penny's very accurate volumetrical process. The burette employed was graduated to cubic millimetres. Pure zinc was used to reduce the iron before adding the standard solution. When the ore contained both oxides of iron, precautions were taken to prevent the action of the air on the solution whilst the ore was dissolving.

5. All the other ingredients of the ore were determined in the manner described under Method No. I.

In all cases the actual weights of the substances obtained during the analysis were given, so that corrections may be made should the atomic weights at present in use be altered at any future time.

Experiments on the Determination of Peroxide and Protoxide of Iron when they exist together in an Ore.—Extremely unsatisfactory results having been obtained by the use of Fuchs's process, some experiments were made with weighed quantities of the pure materials. The copper used was electrotype copper; the iron was in the state of peroxide prepared by precipitation and ignition. The hydrochloric acid was of known strength. The experiments were made in stoppered bottles filled with the liquid to exclude the air.

4·17 grs. of peroxide of iron were dissolved in twice the amount of acid required for complete solution, and poured into a stoppered bottle, containing a piece of sheet copper presenting about 3 square inches of surface. The stopper was tied down with caoutchouc, and the whole left at the ordinary temperature till the solution became nearly colourless. About 16 days were required. The copper was then washed, first with a hot solution of common salt, and afterwards with pure water. It had lost 3·26 grs., whereas it ought to have lost 3·29 had the whole of the produced chloride of copper been converted into dichloride. The bulk of the liquid was about an ounce and a quarter. Similar experiments with twice and ten times the above amount of acid yielded like results; as also did an experiment in which 30 grs. of chloride of sodium were used instead of excess of acid to dissolve the dichloride as it formed.

Similar experiments were made at 100° C., with like results, only that the change, which at the ordinary temperature takes many days, is effected in a few hours.

3·39 grs. of peroxide of iron, dissolved in twice the amount of acid

requisite for solution, were treated exactly as above, except that the bottle was kept in a bath at 100° C. The solution became colourless in a few hours, and the copper was found to have lost 2·74 grs., whereas it ought to have lost 2·68. A similar experiment, in which five times the requisite amount of acid was employed, and another in which 20 grs. of chloride of sodium were employed, instead of excess of acid, also yielded results which were nearly accurate. It was found, however, that when this process was applied to the analysis of the ores it sometimes did not yield such accurate results.

Margueritte's volumetric method was used once or twice, but laid aside in favour of Dr. Penny's, owing to the trouble of preparing the solution, and keeping it of known strength. The solution of bichromate of potash employed was much weaker than that employed by Dr. Penny. To show the accuracy of this process, some of the experiments which were made for the purpose of testing it are given. They are quoted without selection, being just in the order in which they were made. The iron employed was fine iron wire. Quantity taken, 4·025; found, 4·050: taken, 2·90; found, 2·91: taken, 4·29; found, 4·285: taken, 6·51; found, 6·505: taken, 4·10; found, 4·07: taken, 5·35; found, 5·37: taken, 4·77; found, 4·77 grs. The mean error of the seven experiments was rather more than 0·01 gr. of iron.

Fusing Iron Ores with Bisulphate of Potassium.

On attempting to dissolve hæmatite and other iron ores in hydrochloric acid, a certain residue remains; and instead of having recourse to fusion with carbonate of sodium to separate the silica and iron, fusion with bisulphate of potassium at a dull red heat may be employed, which converts the iron into a sulphate, leaving the silica beautifully white. The time is, for 1 grm. of mineral, about 10 to 15 minutes.

Preservation of Proto-Salts of Iron.

Protosulphate of iron may be preserved from oxidation by placing with it a piece of camphor wrapped in clean dry paper.

Protochloride of iron may be obtained pure by evaporating the recent solution almost to dryness, and adding powdered iron and strong hydrochloric acid in the proportion of one part of the former to five of the latter; the mixture is then evaporated to dryness with continued stirring by an iron spatula. The nascent hydrogen evolved effectually reduces all the sesqui- to the proto-chloride, and the dry salt will keep for a considerable time.

Separation of Iron from Aluminium.

Wöhler's process, which we have used with success for many years, is to neutralise the very dilute solution of these two bases with carbonate of sodium, then add hyposulphite of sodium, and, finally, heat till no more

sulphurous acid is disengaged. In this manner all the alumina collects together into a precipitate, which may be calcined. The iron remains in the liquor, which should be concentrated and then decomposed with chlorate of potassium and hydrochloric acid. After filtration to remove sulphur, precipitate the sesquioxide of iron by ammonia.

Mr. Parnell describes a method very similar to the above, as being in use in some continental laboratories. To the slightly acid solution of the oxides a solution of hyposulphite of sodium is added, more than equivalent to the amount of free acid present. The liquid is then boiled in a flask for about ten minutes or a quarter of an hour. The whole of the alumina will be thrown down in a fine granular state, together with the sulphur resulting from the decomposition of the hyposulphurous acid; while the whole of the iron will remain in solution. The liquid is then rapidly filtered, and the precipitate washed with boiling water, dried, ignited in a porcelain crucible, and weighed in the usual manner. The filtrate containing the iron is treated with hypochlorite of sodium, nitric acid, or other oxidising agent, and the iron estimated by precipitation by ammonia and weighing as sesquioxide. Care should be taken to avoid large excess of acid in the first instance, and also, subsequently, of the hyposulphite; the smaller the proportion of sulphur with the precipitated alumina, the more easily may it be filtered off from the iron solution. After calcination, the alumina appears as a perfectly-white, crystalline powder, much resembling precipitated and calcined silica.

The method of weighing the two oxides together, and then separating the alumina by fusion with caustic soda and subsequent treatment with water, is accurate but troublesome. The plan of effecting the separation of the iron by means of sulphide of ammonium from the ammonio-citrate solution of the oxides does not give perfectly accurate results, since the sulphide of ammonium has the power of holding up small quantities of iron in solution; this may be proved by letting the perfectly-clear filtrate stand a few days, when small flakes of sulphide of iron will be deposited.

Another excellent plan to separate iron and aluminium is to put the calcined precipitate of the two oxides in a porcelain boat, and introduce it into a tube of the same material, heated to bright redness, and traversed by a current of dry hydrogen, which is kept up whilst the tube is cooling. The hydrogen is then replaced by a current of gaseous hydrochloric acid, and the tube being re-heated, the iron, reduced by the hydrogen, is converted into a volatile chloride, whilst the alumina is left behind and may be weighed. (See the chapter on Silicates).

Separation of Iron from Zinc.

If the presence of barium is not objectionable, add carbonate of barium to the nearly neutral solution of zinc and sesquioxide of iron. The whole

of the sesquioxide of iron will be precipitated, leaving all the zinc in solution. Or, the solution may be nearly neutralised with carbonate of sodium, and after acetate of sodium is added in excess, brisk ebullition will bring down all the iron as basic acetate. From the filtrate, acidified with acetic acid, a stream of sulphuretted hydrogen will precipitate the zinc.

Separation of Iron from Uranium.

When, as is generally the case, carbonate of ammonium is employed for this separation, it is well known that some of the iron is always dissolved with the uranium. The following is, however, a method for rendering the separation complete:—As oxide of uranium in solution in carbonate of ammonium is not precipitated by sulphide of ammonium, add to the liquid, separated by filtration from the bulk of the oxide of iron, a few drops of sulphide of ammonium to eliminate from it, in the state of sulphide, the small quantity of iron which has been dissolved. After filtering again, a solution is obtained containing all the uranium without any trace of iron.

Separation of Iron from Chromium.

When the iron is in very large excess, the following is a good method for separating the chromium:—Treat the metal or ore by the ordinary processes, to separate the silica, and obtain a liquid containing all the metals in solution, and in which the iron is at its maximum of oxidation; then precipitate the liquid by an excess of a strong solution of potash; and pour, drop by drop, into the solution containing the precipitate, and heated to 80° or 90°, a dilute solution of permanganate of potassium until the permanganate loses its colour; the reaction is terminated when the liquid takes a greenish tinge, owing to the presence of manganate of potassium. Then filter, and saturate the filtered liquid with acetic acid, which immediately reduces the small quantity of manganate of potassium that gave to the solution its green colour. Into the liquid, which frequently has a yellow tinge, pour acetate of lead, which determines a yellow precipitate of chromate of lead, if the least trace of chromium be present.

Another method is to nearly neutralise the solution, containing chromium and peroxide of iron, with carbonate of sodium, and add acetate of sodium in excess. A current of chlorine gas or addition of chlorine water then readily converts the whole of the chromium present into chromic acid. Upon now boiling the solution, the excess of chlorine is expelled, whilst, at the same time, the iron is precipitated as basic acetate. The chromic acid in the filtrate may either be reduced with alcohol and hydrochloric acid, and the sesquioxide of chromium precipitated with ammonia, or acetate of lead may be added and the chromate of lead collected.

If it is not desired to precipitate the iron as basic acetate it may be precipitated with ammonia; all the chromium will remain in solution as chromic acid.

Valuation of Chrome-Iron Ores.

Half a gramme of the finely pulverised ore is taken and fused in a platinum crucible with three times its weight of bisulphate of potassium for one hour; then allowed to cool, and the same amount of a mixture of equal parts of nitrate of potassium and carbonate of sodium put on the top, and again fused for another hour, allowed to cool, and digested in a porcelain dish for two or three hours with water on the sand-bath. Then filtered and well washed out with boiling water. The filter is treated with hydrochloric acid for two or three hours in a warm place until the sesquioxide of iron is dissolved; filter again, and if there is not too much undecomposed ore remaining, it can be weighed and deducted, or if too much remains it must be again fused as before. The chromic acid solution is warmed, and carbonate of ammonium added to precipitate any silica, aluminium, or calcium in solution; it is allowed to stand an hour and filtered; hydrochloric acid is then added to the solution until it is acid; it is next warmed, and sulphurous acid is added to reduce the chromic acid to sesquioxide; ammonia is then added, and the whole is allowed to stand twelve hours, after which it is filtered, the sesquioxide of chromium washed by decantation, dried, ignited, and weighed.

Dr. Genth, of Philadelphia, who has had much experience in the analysis of chrome-iron ore, gives the following process; it is very trustworthy, although long and somewhat tedious.

Of the chrome ore, reduced to an impalpable powder, put 0·5 gramme in a platinum crucible about two inches high, nearly 1¾ inches wide, and holding 52 grammes of water, and place upon it 6 grammes of pure fused bisulphate of potassium, and heat with the greatest care for about 15 minutes, at a temperature scarcely above the fusing point of the bisulphate; then the heat is gradually raised, but not higher than to make the bottom of the crucible red hot, and kept at this temperature from 15 to 20 minutes. Never permit the mass to rise to half the height of the crucible. (If the fusion with bisulphate of potassium is done too rapidly, a portion of the analysis is very apt to be lost by spattering, from the escape of sulphurous acid, resulting from the oxidation of the ferrous oxide by the sulphuric acid). The mass begins now to fuse quietly, and vapours of sulphuric acid go off more freely; it should then be kept at red heat for about twenty minutes, and the heat next raised as high as necessary to drive off the second equivalent of sulphuric acid, and even to decompose a portion of the sulphates of ferric and chromic oxides. To the fused mass add about three grammes of

pure carbonate of sodium, and fuse the mixture, and then, by degrees, keeping the temperature for about one hour at dull red heat, about the same quantity of saltpetre; next heat for fifteen minutes at a bright red heat. The fused mass is dissolved in boiling water, filtered whilst boiling, and washed with boiling water.

The insoluble residue, containing the greater portion of the silicic acid, titanic acid, and alumina, the sesquioxide of iron, zirconia, and—if the fusion has been conducted at a temperature sufficiently high to convert the saltpetre into caustic potash, and the above precautions have been used—all the magnesia, is re-dissolved in dilute warm hydrochloric acid, which generally dissolves it readily and completely, and rarely leaves undecomposed ore behind; but if so, this residue must invariably be fused in a small crucible as before, adding, after the separation of the insoluble portion, the solution containing the small quantity of chromic acid to the first filtrate. (The certainly less troublesome method, to deduct the insoluble portion from the original weight, is bad; such residues have never the composition of the original ore.) The filtrate contains the whole quantity of the chromium as chromic acid, sometimes a trace of manganic acid, small quantities of silicic acid, alumina, and rarely titanic acid. To this solution add an excess of nitrate of ammonium, and evaporate over a water-bath nearly to dryness, and until all the liberated ammonia has been expelled. The precipitate, remaining on addition of water, contains the silicic acid, titanic acid, alumina, and manganic oxide, which had gone into solution with the chromic acid; it is filtered off, and the filtrate made strongly acid with sulphurous acid, carefully heated to boiling, precipitated with a slight excess of ammonia, boiled for a few minutes, and filtered. Dr. Genth says he formerly acidulated the chromic acid solution by hydrochloric acid, and then added sulphurous acid, but he several times observed that, although an excess of sulphurous acid had been used, a small portion of the chromic acid escaped reduction, the filtrate from the ammonia precipitate being yellow. He has in vain tried to find the reason for this singular behaviour. Since using sulphurous acid only, he has never been troubled with anything similar.

It is exceedingly difficult to wash out the chromic oxide; it succeeds best in the following way:—After the precipitate has settled, the clear liquid is passed through the filter, then boiling water is added to the precipitate, and after settling, the supernatant liquid is filtered; the precipitate then is put on the filter, and washed twice or three times with boiling water; it is then washed back again into the dish and boiled with water, until the little lumps which clog together are completely broken up, and it is then filtered again, and this operation repeated until the wash-waters do not show the presence of any sulphates when tested with chloride of barium. The

precipitate is then dried and burned. No matter how well it may have been washed, it almost invariably contains minute quantities of alkalies, in the presence of which a little chromic oxide is converted into chromic acid. The ignited precipitate is therefore put into a dish, boiled with water, a few drops of sulphurous acid added, precipitated by ammonia, filtered, washed, dried, ignited, and weighed.

In this manner the chromic oxide is obtained quite pure, and repeated analyses of the same sample of ore never vary 0·25 per cent of chromic acid.

Mr. O'Neill's process is more expeditious than the above, but is not so accurate, as the results cannot be relied upon much within one per cent. He proceeds as follows:—A fair sample is taken, and reduced to a tolerably fine powder in an iron mortar. Weigh 6 grains of this upon a common balance, and grind in an agate mortar, taking 2 grains only at once; the grinding requires twenty minutes. It is sufficiently ground when all gritty sound or feeling has disappeared, and the ore forms flat cakes rising under the pestle. The success of the analysis depends altogether upon the grinding, which must be scrupulously attended to; the caking mass of ore must be several times swept together with a trimmed quill or a stiff hair pencil, and spread out again with the pestle, so as to thoroughly crush every particle. The ground ore is then placed in a balanced watch-glass, and 5·1 grains of it taken. The usual qualities of ore are very little hygrometric, and present no difficulties in weighing.

Prepare bisulphate of potassium by acting upon pure sulphate of potassium with sulphuric acid, fusing the whole at a red heat in a platinum capsule, and pouring to cool on a stone slab. Sixty grains of this are coarsely pulverised and placed in a platinum crucible, so large that the bisulphate when fused only rises one-fourth its height. The ore is then swept on the bisulphate, lightly mixed with it by means of a wire, and the whole exposed to heat for twenty minutes. The mass must be maintained in perfect and quiet fusion for ten minutes; for the first few minutes care must be taken that the fused mass does not rise over the edge of the crucible. When cooled, the mass must be detached by gently pressing the sides of the crucible and received into a porcelain dish, where it is treated with water until entirely dissolved or disintegrated. If the mass comes out of the crucible in a solid lump, this solution will take a considerable time. To avoid this inconvenience take the red-hot crucible with a forceps, and cause the molten mass to flow round the sides, where it cools in a thin crust, easily detached from the crucible, and readily acted upon by water.

Carbonate of sodium is added to the acid mixture until it is strongly alkaline; the precipitate is thrown upon a filter and slightly washed; then drained and dried as quickly as possible. If there be any ore unacted upon, it

is visible here as a heavy, black, crystalline, or granular powder, easily discernible in the white dish. If the grinding is properly performed there ought never to be a trace of this black powder visible.

A mixture is made of two parts by weight of powdered chlorate of potassium and three parts of pure dry carbonate of sodium; 70 grains of such a mixture is taken, and the greater portion thrown into a small glass mortar. The dried precipitate is detached as much as possible from the filter, allowing it to fall on the mixed carbonate and chlorate. The filter is then carefully burned, and the ashes added to the contents of the mortar; the precipitate is carefully mixed up with the alkaline and oxidising mixture, by means of a glass pestle, and the whole transferred to a platinum crucible; the remaining chlorate and carbonate serve to rinse out the mortar. The whole is mixed up with a wire, and exposed to a gradually-increasing heat until in perfect fusion, and kept so for ten minutes; the whole time of heating is from twenty to thirty minutes. Some ores, which contain a good deal of magnesia and silica, are difficult to fuse, and require the heat of a muffle, but for ordinary ones a Bunsen's burner suffices very well, and twenty minutes is long enough for the fusion. The fused mass is cooled, dissolved in hot water, and filtered from the oxide of iron, &c., the filter being well washed. Any undecomposed ore remaining will be found on the filter, and may be rendered visible by boiling its contents with hydrochloric acid. The substitution of chlorate of potassium for nitrate is rendered necessary by the subsequent method of determining the chromic acid in solution. With nitrate of potassium there is nearly always production of alkaline nitrite, or some other compound of the lower oxides of nitrogen, which causes the evolution of nitric oxide upon addition of acid, and the consequent partial or total reduction of the chromic acid. Chlorate of potassium is easily and wholly decomposed by heat.

Mr. O'Neill uses a volumetrical method to estimate the chromic acid, depending upon the capability of sulphurous acid to deoxidise chromic acid at the ordinary temperature in presence of free sulphuric acid. Prepare a strong solution of bisulphite of sodium, by passing sulphurous acid through caustic soda to saturation, and then make it alkaline with caustic soda, so as to have a neutral sulphite, which is less readily oxidised by keeping than the bisulphite. Use a dilute solution made from this concentrated sulphite, of such a strength that one grain of pure bichromate of potassium requires about, and not less than, 200 grains measure of the sulphite to deoxidise it. The value of the sulphite must be determined for every operation, since it is continually absorbing oxygen. This is done twice by weighing out three grains and four grains of pure bichromate, dissolving each of them in ten ounces of water and acidulating freely with sulphuric acid, then adding the sulphite from the burette, with continual

stirring, until the chromic acid is destroyed. The stopping-point may be ascertained by the colour when one is accustomed to the reaction, but even an experienced eye will often be glad of additional evidence. A mixture of iodide of potassium and boiled starch, slightly acidulated, forms a delicate test; it has usually a faint colour, which is even preferable to a colourless mixture. An exceedingly small quantity of chromic acid developes the blue colour in spots of this mixture, and a very slight excess of sulphite makes it colourless. One division of the sulphite test-liquor, or 0·05 grain of bichromate of potassium in twelve ounces of water, easily and quickly influences the test mixture. The chromate from the chrome ore is tested in the same manner, and the quantity of oxide of chromium or chromic acid calculated from the equivalents of bichromate of potassium. The tenth of a grain more than five is taken to allow for all losses, and the results are multiplied by twenty for the percentage. 151 of bichromate of potassium is reckoned equivalent to 80 of green oxide of chromium, and 104 of chromic acid. A determination can be made by this process in three or four hours, and a double determination in a little longer time.

Mr. P. C. Dubois has found that finely-pulverised chrome-iron ore may be completely resolved by fusing it at a red-heat for ten or fifteen minutes over a blast lamp with four or five times its weight of fluorhydrate of potassium. The fused mass has a clear green colour. By treating this with sulphuric acid until the whole of the fluorine is expelled, and then adding water, the chromium, iron, and aluminium are completely dissolved as sesqui-salts. The easiest method of separation is the following:—To the solution an excess of caustic soda is added, after which, without filtering, chlorine gas is to be passed through until the sesquioxide of chromium is converted into chromic acid. The solution is then to be heated to expel excess of chlorine, nitric acid added in slight excess, and the sesquioxide of iron and alumina precipitated by ammonia. To the filtrate acetic acid is to be added in small excess; after which the chromic and sulphuric acids may be precipitated together by acetate of lead. The precipitate, after washing, is to be boiled with hydrochloric acid and alcohol, the lead separated as chloride, and the chromium determined in the usual manner as sesquioxide. This method gives a complete separation, even when magnesium and nickel are present in the ore.

Volumetric Valuation of Chrome-Iron Ore.

The following method for quickly and accurately determining the amount of chromium and iron in chrome-iron ores, is given by Mr. J. Blodget Britton:—Reduce the mineral to the finest state of division possible, in an agate mortar. Weigh off 0·5 grm. and add to it 4 grms. of a flux, previously prepared, composed of one part chlorate of potassium and three parts soda-

lime; thoroughly mix the mass by triturating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright red heat for an hour and a half or more. The mass will not fuse, but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and turn the powder into a tall 4 oz. beaker and add about 18 c.c. of hot water, and boil for two or three minutes; when cold, add 15 c.c. of hydrochloric acid of common strength, and stir with a glass rod for a few minutes, till the solid matter, with the exception, probably, of a little silica in a flaky gelatinous state, becomes dissolved. Both the iron and chromium will then be in the states of sesquioxide of iron and of chromic acid. Pour the fluid into a white porcelain dish of about 20 ozs. capacity, and dilute with washings of the beaker to about 3 ozs. Immediately after, also, pour cautiously into the dish 1 grm. of metallic iron of known purity, previously dissolved in dilute sulphuric acid and further diluted with cold water to about 5 ozs., to make up the volume in the dish to about 8 ozs.

Use for this purpose fresh borings from a piece of bar iron, containing less than 0·05 of foreign matter, dissolved in 18 c.c. of dilute sulphuric acid of 1 part acid and 3½ parts water, in a tube 12 inches long and ⅝ inch diameter, closed at the top with an india-rubber stopper perforated for a ¼ inch tube, bent short round at right angles, and extending horizontally about 3 or 4 inches, applying heat to expel atmospheric air and facilitate operations.

When the iron is dissolved, and having ascertained that the solution is free from sesquioxide, nearly fill the tube with *cold* water and cautiously pour the contents into the dish and add about two tubes-full more of *cold* water to make up the solution to about 8 ozs., and then determine, volumetrically, with a standard solution of permanganate of potassium, the amount of protoxide of iron remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidised to sesquioxide by the chromic acid. Every one part so oxidised will represent 0·320 of metallic chromium, or 0·4663 of sesquioxide, in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be determined, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder, as already directed, dissolve it in a tube of the kind described, by adding, first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of hydrochloric acid, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure sheet zinc cut in small strips, sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease, and the

zinc has become quite dissolved; then nearly fill the tube with cold water, acidulated with 1-10th of sulphuric acid, and pour the contents into the porcelain dish, and add cold water to make up the volume to about 8 ozs., and complete the operation with the standard permanganate solution.

The process, if conducted as directed, affords very accurate results; upon repeating the determinations there should be practically no variation. The whole time consumed need not exceed three hours to determine both the chromium and the iron, if the two ignitions are proceeded with simultaneously. Fine iron wire may, in most cases, be used with greater convenience than borings. Mr. Britton, however, prefers the latter, and keeps in the laboratory for use a large piece of iron of the kind mentioned, from which, by the aid of a small foot-lathe, he obtains in a moment or two clean unoxidised borings whenever they are needed, and thus has an unalterable standard always at hand.

For dissolving minerals and metals, tubes of the kind described, though sometimes of a larger size, are generally preferable to all other vessels, for many reasons:—avoidance of loss of substance, convenience of rinsing, expulsion of air while digesting and boiling, carrying out of the laboratory all of the evolved gases by means of the small bent tubes leading into a chamber connected with the main chimney, &c.

Dr. Wolcott Gibbs has shown that chrome-iron ore may be completely resolved by fusion with fluohydrate of fluoride of potassium. In this and in all similar applications of the fluohydrate it is best to evaporate the finely-pulverised mineral to dryness with a concentrated solution of the salt. On subsequently heating to low redness, the resolution of the mineral is effected with the utmost ease, a portion of the chromium being usually oxidised to chromic acid by the oxygen of the air. After expelling the fluorine by heating the fused mass with sulphuric acid, the remaining mass is dissolved in water, rendered nearly neutral by a solution of carbonate of sodium, and acetate of sodium is added in excess. A current of chlorine gas, or a solution of chlorine water, then readily converts the whole of the chromium present into chromic acid, especially when the solution is hot, and when it is kept nearly neutral by occasional addition of carbonate of sodium. The excess of chlorine is easily got rid of by boiling.

The iron and aluminium may then be precipitated together by boiling the solution in the presence of excess of acetate of sodium. It is more convenient and equally accurate to neutralise the solution with ammonia, separate the sesquioxide of iron by filtration, and determine the chromium in the filtrate by reduction and precipitation with ammonia.

Chrome-iron ore can also be readily broken up by Professor Storer's plan of oxidising with chloride of potassium and nitric acid (page 54). The following experiment shows the value of this method, but no further trials

have as yet been made to test its applicability to quantitative analysis. A small quantity of chrome-iron ore was ground to very fine powder, and treated, in a dish, with nitric acid and chlorate of potassium, as before described. At the end of half an hour, that portion of the ore which still remained undissolved was washed with water, dried, fused with a mixture of carbonate of sodium and nitrate of potassium, and the fused mass boiled with water; the solution thus obtained gave no reaction for chromium when tested for that substance.

Separation of Iron from Zirconium.

Render the solution nearly neutral with carbonate of sodium, and add excess of hyposulphite of sodium. Boil the liquid for a short time and all the zirconia will be precipitated, mixed with a little sulphur, but perfectly free from iron, which will all be in solution.

The solution containing zirconium and iron may also be boiled with nitric acid to peroxidise the iron, and then precipitated with excess of ammonia. The precipitate is then digested with excess of oxalic acid, which dissolves the whole of the iron together with a trace of zirconia, but leaves the greater part of the zirconia in the form of an insoluble oxalate.

Or, the mixed precipitate of sesquioxide of iron and zirconia may be digested in sulphide of ammonium until the whole of the iron is in the state of sulphide. Decant the supernatant liquid and digest the black precipitate in a dilute solution of sulphurous acid. This dissolves the sulphide of iron and leaves the zirconia quite colourless.

The process given on p. 50 for the preparation of pure zirconia, &c., may also be used to separate iron and zirconium.

Separation of Iron and Titanium.

When sesquioxide of iron and titanic acid are together in dilute solution, they can be separated by ebullition with hyposulphite of sodium, as in the case of iron and zirconium. The titanic acid precipitates whilst the iron remains in solution. Or, add ammonia in excess to the solution, digest the mixed precipitate of titanic acid and sesquioxide of iron with sulphide of ammonium, and then dissolve out the iron with sulphurous acid.

Other methods of separating iron and titanium may be found under the heading Titanium, p. 46, or under the description of the method of analysing titaniferous iron ore (p. 110), and estimation of titanium in iron and steel (p. 104).

Volumetric Estimation of Iron and Titanium.

The amount of titanium and iron in a solution may be estimated volumetrically in the following manner:—Add metallic zinc to the slightly acid

solution until the titanium is reduced to the state of violet sesquioxide and the iron to protoxide. Then decant from the zinc, and add from a burette a standard solution of permanganate of potassium until the violet colour disappears, finding the moment at which the iron begins to oxidise in its turn by taking from time to time a drop of the liquid and mixing it with a drop of sulphocyanide of potassium in a porcelain capsule. When the sulphocyanide begins to be coloured, the number of divisions used will give the quantity of titanic acid; the operation may then be continued in the usual manner for estimating the iron.

Another method consists in reducing the iron by sulphuretted hydrogen or sulphite of sodium, which does not act on the titanic acid, and then estimating the iron after having freed the liquid from the excess of sulphuretted hydrogen or sulphurous acid in the usual way. The difference gives the amount of titanium. The former method is the more accurate of the two, as the latter frequently gives too much iron.

Separation of Iron from Cerium.

The metals must be in solution in the form of sulphates. Reduce the iron completely to the form of protosulphate by means of a current of sulphuretted hydrogen passed into the hot solution. To the solution, which should be concentrated, add a saturated solution of sulphate of sodium, together with a sufficient quantity of the dry sulphate in powder to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sulphates of sodium and the cerium metals separate immediately, as a white, highly crystalline powder, which is to be thrown upon a filter and thoroughly washed with a hot saturated solution of sulphate of sodium. After washing, the double sulphates upon the filter are to be dissolved in hot dilute hydrochloric acid, the solution largely diluted with water, and the cerium metals precipitated by oxalate of ammonium in the manner already pointed out (p. 41). From the filtrate the iron may be precipitated at once as sesquioxide by ammonia, after peroxidising it by means of chlorine water, and rendering the solution slightly acid with hydrochloric or sulphuric acid.

Separation of Iron from Magnesium.

When sesquioxide of iron is precipitated by means of ammonia from a solution containing magnesium, some magnesia is always carried down with it in spite of the presence of an excess of ammoniacal salts. They may, however, be perfectly separated in this manner:—dilute the solution considerably, neutralise with carbonate of sodium, then add acetic acid and acetate of sodium to the cold solution. Boil for a short time, when the whole of the iron will be precipitated as basic acetate. Filter hot and wash quickly with hot water. All the magnesium will be in the solution.

Dr. Calvert dissolves the oxides in hydrochloric and a little nitric acid, nearly neutralises with ammonia, and precipitates the iron with succinate of ammonium. The succinate of sesquioxide of iron is rapidly filtered off and washed with cold water. The filtrate will contain the whole of the magnesium.

Separation of Iron from Calcium.

When sesquioxide of iron is precipitated in the ordinary manner with ammonia in the presence of excess of ammoniacal salts, it always carries down a considerable quantity of lime, if this earth is present, and the larger the proportion of iron as compared with that of calcium, the greater is the proportion of calcium carried down by the iron. This error can be avoided by precipitating the iron as succinate, or by throwing the iron down as basic acetate as before described (Separation of Iron from Magnesium). In either case the wholeof the calcium will remain in the solution.

Sesquioxide of iron may be safely precipitated by ammonia if the precaution is taken to boil until all smell of ammonia has gone off, before filtering; the iron does not now retain any calcium. If much calcium be present a little chloride of ammonium may be added to make sure of getting all into solution. As the solution no longer contains free ammonia, it can be filtered without there being danger of the calcium coming down as carbonate by absorption of carbonic acid from the atmosphere. The filtrate may be concentrated by evaporation, and the calcium precipitated as oxalate.

CHAPTER VI.

MANGANESE, NICKEL, COBALT.

MANGANESE.

Estimation of Manganese.

UNDER many circumstances manganese can be determined with great accuracy by precipitation as ammonio-phosphate, and weighing as pyrophosphate, like magnesium. This salt, from its highly crystalline structure, the facility with which it is formed, and its insolubility, appears well adapted to the quantitative estimation of manganese. Dr. Wolcott Gibbs, who has worked out this method, recommends that to the solution of manganese, which may contain salts of ammonium or of the alkaline metals, di-sodic ortho-phosphate is added in large excess above the quantity required to precipitate the manganese as ortho-phosphate. The white precipitate is then to be re-dissolved in excess of sulphuric or hydrochloric acid, heated to the boiling-point, and ammonia added in excess. A white or semi-gelatinous precipitate is produced, which, on boiling or standing for some time, even in the cold, gradually becomes crystalline, and finally is completely converted into beautiful talcose scales which have a pearly lustre and a pale rose colour. It is best to precipitate each time in a platinum vessel, in which the ammonio-phosphate may be boiled for ten or fifteen minutes, and to allow the salt to remain at a temperature near the boiling-point of the liquid for an hour after it has become crystalline. The ammonio-phosphate may then be filtered off and washed with hot water. The washing takes place with extraordinary facility on account of the crystalline character of the salt. The ortho-phosphate, after drying and ignition, yields pyrophosphate of manganese as a nearly white powder.

The advantage of this method over that commonly employed for the estimation of manganese, is that the process admits of the metal being weighed in the form of a perfectly definite compound, and not as an oxide which cannot be safely assumed to be manganoso-manganic oxide. When manganese is associated with the alkaline earths, it is, of course, first to be separated as sulphide, or as a hydrate of the sesquioxide. The ammonio-phosphate is almost absolutely insoluble in boiling water, in ammonia, and in solutions of salts of ammonium. The salt is nearly white, but sometimes

becomes a little more red upon the filter. If it assumes a rather deep dull red colour, the whole of the phosphate of manganese has not been converted into ammonio-phosphate. The precipitate is then to be re-dissolved in dilute hydrochloric acid, more phosphate of sodium added, and then ammonia in excess, after which the boiling is to be repeated. This repetition is very rarely necessary, a little practice enabling the analyst to judge when the conversion from the flocky-gelatinous to the crystalline condition is complete. The filtrate from the crystalline salt is perfectly free from manganese. This process will not give accurate results in the presence of copper, or of metals which form precipitates with phosphates (see p. 104). Phosphoric acid cannot be determined in this way by precipitation as ammonio-phosphate of manganese, because the crystalline character of the salt upon which the success of the process depends is only produced by digestion with an excess of phosphate.

Manganese may be determined by precipitation as oxalate, and subsequent titration with permanganate of potassium (see p. 63, Leison's process for the estimation of zinc). To a soluble salt of manganese add oxalic acid, and then a large excess of strong alcohol; oxalate of manganese is completely precipitated. The subsequent filtration and titration with permanganate of potassium is conducted as described at p. 63. From the amount of oxalic acid thus found the quantity of manganese may be caculated.

A. Guyard estimates manganese by precipitation with permanganate of potassium, which forms, with salts of protoxide of manganese, a precipitate of permanganate of protoxide of manganese, insoluble in water and dilute inorganic acids. All the other metals whose protoxides react on permanganate of potassium are found in the state of peroxide in the same liquor in which the manganese exists as protoxide; consequently, these foreign metals, whatever they may be, do not interfere with the results. As long as there is manganese in the liquor it is precipitated, and the permanganate of potassium is decolourised; but as soon as the reaction is ended a drop of the permanganate communicates a persistent rose tint to the solution.

The operation is best performed in the following manner:—One or two grammes of the salt or manganese to be assayed are dissolved in aqua regia. The solution is boiled for some time to transform all the manganese into a salt of protoxide; the solution is then very nearly neutralised by an alkali; that done, it is diluted with a large quantity of boiling water, and the whole is kept at a temperature of about 80° C. The standard solution of permanganate of potassium is now gradually added from a burette. The manganese is immediately precipitated in the form of violet-brown flocculi of permanganate of manganese, of the formula—

$$3MnO,Mn_2O_7,5HO = 5MnO_2HO.$$

The operation is arrested occasionally to allow the precipitate to collect, which it does very quickly; and is entirely stopped when a persistent rose colour is obtained.

To determine the strength of the solution of permanganate of potassium use pure sulphate of the protoxide of manganese dried at rather a high temperature. This salt has then a fixed composition, and keeps well in a well-stoppered bottle. A normal solution may also be prepared for each operation.

For every equivalent of permanganate of potassium added three equivalents of protoxide of manganese will be precipitated. In any case the solution must be so prepared that 30 c.c. correspond to about 1 gramme of manganese.

The permanganates of the protoxide of manganese are three in number:—

1.	The oxide Mn_7O_{12}, the formula of which should be written	$5MnO,Mn_2O_7$.
2.	" Mn_6O_{11} " " "	$4MnO,Mn_2O_7$.
3.	" Mn_5O_{10} " " "	$3MnO,Mn_2O_7$.

Each of these bodies is formed, according as we mix 1 equivalent of permanganate of potassium with 5, 4, or 3 equivalents of a salt of the protoxide of manganese. The first is formed in the cold when there is more salt of manganese than permanganate of potassium; the second is also formed in the cold when more permanganate than salt of manganese is present in the solution. The binoxide is only formed in a hot solution.

Valuation of Manganese Ores.

The best methods used for the valuation of manganese ores are not necessarily those which give in the most rapid and accurate manner the absolute amount of peroxide of manganese present in the ore. The analyst must bear in mind that the commercial value of manganese ore depends on its power of liberating chlorine from hydrochloric acid; and it not unfrequently happens that an ore, which on accurate analysis would be reported to contain a high percentage of peroxide of manganese, likewise contains some other mineral (protoxide or magnetic oxide of iron), which will materially reduce the value of the manganese as a chlorine-yielding ore. It is on this account that some processes—excellent though they be from a purely analytical point of view—have fallen into discredit amongst manufacturers, whilst other processes which do not profess to give the amount of peroxide of manganese *actually* present, but only that *available* for liberating chlorine, are now generally adopted. In the following pages are given the methods of testing manganese ore for the available peroxide which have best stood the test of practical experience.

Messrs. Sherer and Rumpf, after examining all the most approved

methods in Dr. Fresenius's laboratory at Wiesbaden, have come to the conclusion that Bunsen's method is the best for rapidly giving the amount of available manganese in an ore. This process is carried out by dissolving a weighed quantity of the sample in strong hydrochloric acid in a small flask, until complete decomposition has taken place. The escaping chlorine is received in a strong solution of iodide of potassium, and the liberated iodine subsequently estimated by means of a standard solution of hyposulphite of sodium and a solution of starch. To prevent the solution of iodide of potassium from being sucked back into the generating-flask, a few small pieces of magnesite are introduced with the manganese, so that a continual slight escape of carbonic acid takes place through the solution. The solution of hyposulphite of sodium is tested by means of carefully prepared pure iodine, dissolved in iodide of potassium. The solution should be of such a strength that 1000 c.c. of hyposulphite of sodium solution corresponds to from 2 to 3 grms. of peroxide of manganese. In this estimation the iodine liberated by the chlorine should be tested as soon as possible after the decomposition; it gives higher results after standing 24 hours than before. These higher results are caused by the liberation of iodine by spontaneous decomposition of hydriodic acid, set free by hydrochloric acid, distilled over during the process. The following experiment proves this:—A few drops of hydrochloric acid were added to a solution of iodide of potassium. The solution remained for some hours colourless, but, after standing 24 hours, had become quite yellow, and was found to contain free iodine sufficient to indicate 8 per cent of peroxide of manganese when titrated with hyposulphite.

Messrs. Sherer and Rumpf have made the suggestion that the value of manganese ores should be measured by chlorometrical degrees rather than by the actual percentage of binoxide; thus tending in the same direction as the resolution* passed by the Association of Alkali Manufacturers, in 1869, in reference to this subject—a decision which would seem also to indicate a desire on the part of manufacturers that tests of manganese ore should express the amount of peroxide *available* for liberating chlorine, and not the amount *actually* present in the ores.

For the above reasons, Dr. Paul adopts Mohr's method of using a known quantity of a standard solution of oxalic acid, together with excess of sulphuric acid, for dissolving the ore; if necessary, boiling until the ore is completely dissolved, and then, by means of a standard solution of permanganate, determining the quantity of oxalic acid remaining undecomposed. This method is very convenient for testing manganese ores, and involves

* "That, as the testing of manganese according to the method of Will and Fresenius, is, in the opinion of the meeting, incorrect, and yields uncertain results, it is recommended to members of this Association not to buy by that test."

only one weighing for each test. The results obtained are also very uniform.

This method has also the advantage of giving results which fairly represent the amount of available peroxide in manganese ores; for any iron that may be present as metal or protoxide would consume an equivalent quantity of permanganate solution, and thus apparently reduce the quantity of oxalic acid decomposed by the peroxide to an extent proportionate to the amount of iron existing in the ore. Thus, for instance, if the quantity of oxalic acid decomposed by 100 grains of manganese ore free from iron or protoxide of iron were 109·53 grains, the ore would contain 76·5 per cent of peroxide, and the whole of that would be available. But, if the 100 grains of ore also contained 5·6 grains of metallic iron, or an equivalent of protoxide, the permanganate solution required for peroxidising that iron would represent 6·3 grains of oxalic acid, and the quantity of oxalic acid decomposed by the peroxide would appear so much less than it really was, or 103·23 grains instead of 109·53 grains. Accordingly, the amount of peroxide would be represented as 72·1 per cent, instead of 76·5 per cent; and that would, in fact, be the amount of peroxide available for generating chlorine.

This method of testing recommends itself by its simplicity, and by the fact that the standard solutions of oxalic acid and permanganate will keep for a long time without alteration of value. The oxalic acid solution contains 63 grms. in the litre, and 1 c.c. is equivalent to 5 c.c. of the permanganate solution.

Mr. John Pattinson prefers a modification of Otto's process for the valuation of manganese, which consists in boiling the ore with a known weight of a proto-salt of iron, and then estimating the excess of iron by a standard solution of bichromate of potassium. This modified process, in his opinion, requires less skill and care at the hands of the operator than Bunsen's method, as described by Messrs. Scherer and Rumpf. 30 grs. of clean iron wire are placed in a 20 oz. flask, along with 3 ozs. of dilute sulphuric acid, made by adding 3 parts of water to 1 of oil of vitriol. A cork, through which passes a tube bent twice at right angles, is inserted in the neck of the flask, and the flask is heated over a gas flame until the iron is dissolved. The bent tube is placed so as to dip into a small flask or beaker containing a little water. When the iron is quite dissolved, 30 grs. of the finely-pounded and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame until it is seen that the whole of the black part of the manganese is dissolved. The water in the small flask or beaker is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well

rinsed, and the contents of the flask made up to about 8 or 10 ozs. with distilled water. The amount of iron remaining unoxidised in the solution is then ascertained by means of a standard solution of bichromate of potassium. The amount the bichromate indicates, deducted from the total amount of iron used, gives the amount of iron which has been peroxidised by the manganese ore, and from this can be calculated the percentage of peroxide of manganese contained in the ore. Thus, supposing it were found that 4 grs. of iron remained unoxidised, then $30-4=26$ grs. of iron, which have been oxidised by the 30 grs. of ore. By a simple calculation it is found that this 26 grs. of iron are equivalent to 20·43 grs. of peroxide of manganese, the amount of peroxide in the 30 grs. of ore. The percentage is, therefore, 68·10.

It will be seen, from the above description, that the only differences between this method and that usually described in hand-books are the use of sulphuric acid instead of hydrochloric acid, and the dispensing with the use of a stream of carbonic acid. These alterations, however, enable us to get rid of the source of error caused by the evolution and escape of a little chlorine, and also of the somewhat complicated and troublesome apparatus required to supply a stream of carbonic acid.

The use of sulphuric acid instead of hydrochloric acid not only gets rid of the before-mentioned source of error, but it is also the reason why the carbonic acid atmosphere can be dispensed with. It has been ascertained that the solution of iron in sulphuric acid does not oxidise appreciably by exposure to air within any reasonable time; certainly not within the time required to make the test. The solution of iron in hydrochloric acid oxidises much more rapidly.

The kind of iron wire which answers best for these analyses is that used by wire-workers, and known as "annealed iron wire." Only the purest qualities of iron are used for wire of this description. Carefully examined by comparing it with pure oxalic acid and pure bichromate of potash, as well as by heating it in an atmosphere of chlorine, it is found to be within about 0·1 of a per cent of being absolutely pure, so that for all practical purposes of testing it may be considered pure. There is no difficulty in obtaining it in large quantity and of uniform quality. Wire of this kind, of such thickness that 22 wires laid close together cover an inch, is of equally pure quality with that which requires about 85 wires to the inch. The latter is to be preferred because it is more easily cut and dissolved, and it is more likely to be pure. Pianoforte wire, which is made of steel, will not do, excepting a correction is made for the amount of carbon it contains. Mr. Pattinson says that he has found wire of this kind which contains only 98·50 per cent of pure iron. The odour of the hydrogen evolved during solution is a good indication of the purity of the iron. With steel wires the odour of carburetted

hydrogen is very strong, but with the annealed iron wire it is very slight. In all cases it will be desirable to ascertain the purity of every new batch of iron wire obtained previous to its being used for testing manganese ores. Having once obtained wire of known purity, all future batches may be most easily and correctly tested by comparing the amount of peroxide of manganese, and consequently of iron, indicated by a certain ore when tested by the new wire with the amount indicated when tested by the wire of known purity. The wire is easily cleaned from all adhering oxide and dirt by passing it a few times through fine emery paper and afterwards through a cloth. It is dissolved by the sulphuric acid in about fifteen minutes. Crystals of protosulphate of iron, or of the double sulphate of iron and ammonium are not recommended, on account of the uncertainty of their composition, as they are never met with in so pure a condition as the iron wire. Besides, there is no advantage in their use; it is quite as easy to weigh the iron wire as to weigh crystals of protosulphate of iron. A standard solution of protosulphate of iron does not keep sufficiently well to make it worth while to use this.

The use of the small flask or beaker in connection with the bent tube is to prevent all loss of iron by its being carried over with the hydrogen and steam. Occasionally a slight trace of the iron has been thus carried over through the tube, but this is, of course, all arrested by the water in the small beaker or flask, and is again returned into the larger flask when the tube is rinsed out.

The length of time required to decompose the manganese ore depends upon the hardness of the sample under examination, and this mode of testing thus affords a good indication of the nature of the ore in this respect. Soft ores will be decomposed in a minute or two, whilst very hard ores require fifteen minutes or more. The decomposition can be hastened by adding more oil of vitrol, but this must be done after the iron is dissolved, as the latter does not readily dissolve in stronger acid than that above mentioned.

The standard bichromate of potassium solution is made so that 1000 fluid grains will peroxidise 10 grains of iron. It is applied to the diluted solution in the usual way. If there is reason to suppose that the ore to be tested contains more than about 78 per cent of peroxide, it will then, of course, be necessary to use less than 30 grs. of ore or more than 30 grs. of iron; as these quantities are only intended for ores of a lower percentage than about 78.

Referring to the discrepancies in the results of analysis of manganese ore, especially that imported from Spain, which have been noticed, according as the method of quantitative estimation of peroxide of manganese employed was that of Fresenius and Will, or that known as the

iron test, Dr. Mohr says that the cause of this discrepancy is due to a certain amount of magnetic oxide of iron present along with the manganese ore. Since the magnetic oxide of iron interferes in the same manner when such a manganese is employed for the manufacture of chlorine, and since the quantity of the gas set free is only that which remains after the oxidation of the magnetic iron ore, the manufacturer who purchases such manganese is entitled to pay for that article only its value as peroxide of manganese. It, however, frequently occurs that the mining and manufacturing interests here clash, and that, as a consequence, the ore proprietor will desire the value of his material to be estimated by the method of Fresenius and Will, while the manufacturer prefers that of the iron test. That right as well as equity are on the manufacturer's side is clear from the following instance:—Suppose the ore contains a mixture of 1 atom peroxide of manganese and 2 atoms magnetic iron ore, or 27·3 per cent of the former with 72·7 per cent of the latter; in such a mixture the method of Fresenius and Will will indicate with precision the amount of peroxide of manganese, but on adding hydrochloric acid to this mixture not a trace of chlorine will be given off, since the free atom of oxygen of the peroxide of manganese is just sufficient for the oxidation of the 2 atoms of protoxide of iron of the magnetic iron ore; in the same way a mixture of binoxide of manganese with protosulphate of iron or protocarbonate of that metal will be perfectly worthless as an article for chlorine-making use.

Dr. Mohr accordingly recommends that manganese ores and samples of peroxide of manganese should be always tested, previous to analysis, with an astatic magnetic needle, and he further recommends Dr. Bunsen's process (given on p. 141) as the best and surest method of analysis. This process is really the same as that which the manufacturer employs for making chlorine; any magnetic iron ore present will become oxidised in both processes, and a special examination for magnetic oxide of iron is rendered unnecessary, while the available manganese for the production of chlorine only is estimated.

Separation of Manganese from Iron.

Obtain the two metals in the form of chlorides (sesquichloride of iron and protochloride of manganese), dilute the solution considerably, and neutralise as nearly as possible with carbonate of sodium. To the cold solution add acetate of sodium in more than sufficient excess to change all the iron and manganese by double decomposition to neutral acetates. Add a few drops of acetic acid. Raise to the boiling-point and keep in brisk ebullition for a short time, and then filter rapidly through a ribbed filter, keeping the liquid as hot as possible during filtration. The whole of the iron will be in the precipitate as basic acetate, whilst the manganese will be in solution. If an absolutely

complete separation is needed, re-dissolve the precipitate in hydrochloric acid, and repeat the operation. Traces of manganese, which the first precipitate of basic acetate of iron may have carried down, are in this manner removed. The two filtrates containing manganese may be added together.

Succinate of ammonium added to a neutral solution of sesquichloride of iron and protochloride of manganese entirely precipitates the iron. Filter off and wash with cold water; all the manganese will be in the filtrate.

Carbonate of barium added gradually, with constant stirring, to a similar solution, precipitates all the iron as sesquioxide.

To a similar solution, which must be acid and cold, add solution of carbonate of sodium, drop by drop, with constant stirring, till the sesquioxide of iron is entirely precipitated, then filter; the manganese will be held in solution by the excess of carbonic acid in the liquid. Of these methods we have found the one first described the most accurate.

For other methods see p. 101 (Estimation of Manganese in Iron), p. 109 (Analysis of Blister Steel), p. 110 (Analysis of Spathic Iron Ore), and p. 119 (Special Methods for Analysis of Iron Ores).

Separation of Manganese from Aluminium.

Manganese and aluminium may be separated by employing a similar process to the one first described for the separation of manganese from iron (p. 145, with acetate of sodium), bearing in mind that the precaution of dissolving the precipitated basic acetate of aluminium, and re-precipitating it by treatment with acetate of sodium as there advised, should always be adopted, since aluminium has more tendency than iron to carry down manganese.

Another process consists in adding chloride of ammonium, heating to ebullition, pouring in caustic ammonia, and boiling till the excess of the latter is disengaged. The small quantity of protoxide of manganese at first carried down decomposes the chloride of ammonium upon ebullition and dissolves as chloride, the ammonia going off. When no more smell of ammonia is perceived, the solution may be filtered without taking special precautions against free access of air.

Separation of Manganese from Zinc.

Obtain the solutions in the form of protochlorides, nearly neutralise with carbonate of sodium, dilute with a large quantity of hot water, and keep the solution at about 80° C. Add solution of permanganate of potassium until the supernatant liquid is of a persistent rose-colour. All the manganese will be in the precipitate in the form of permanganate of manganese, or

binoxide of manganese, whilst the zinc will be in solution. If the strength of the solution of permanganate of potassium has been previously ascertained, the manganese may be determined in this way quantitatively (see p. 139): if not, the precipitate may be filtered off, calcined, and weighed as Mn_3O_4. Three-fifths of the total quantity of manganese found will represent the amount originally in solution.

Separation of Manganese from Uranium.

This separation may be effected by means of permanganate of potassium in the same way as that of manganese from zinc as above described.

Separation of Manganese from Cerium.

This is best effected in the same way as the separation of iron from cerium (p. 136).

Separation of Manganese from Magnesium.

To separate manganese from magnesium, the best plan consists in adding a solution of acetate of sodium, heating, and passing a current of chlorine through the liquid, when permanganate is formed. Supersaturate with ammonia, and boil, when all the manganese is reduced to sesquioxide and precipitated, whilst the magnesium remains in solution. If there be a large quantity of magnesium present, a certain quantity of sal-ammoniac must be first added.

The same process will serve to separate lime from protoxide of manganese.

NICKEL.

Preparation of Metallic Nickel.

Nickel can easily be precipitated as a coherent metallic sponge, by placing a solution of a pure proto-salt of nickel in contact with metallic magnesium in the form of ribbon. Hydrogen is given off, and if the materials are pure the nickel will likewise be pure. The sponge is to be well washed with hot water, dried, and then compressed in a steel mortar, when it will assume a metallic brilliancy. Nickel precipitated in this manner can be moulded and condensed by pressure into bars, which will be found to possess magnetic properties like iron. This compressed sponge can be melted in a lime crucible before the oxyhydrogen blowpipe (see Iron, p. 68).

Estimation of Nickel.

In precipitating nickel from its solutions by means of sulphide of ammonium, the analyst is frequently troubled by the sulphide of nickel dissolving in the excess of precipitant, colouring it brown. This can be completely avoided by employing sulphide of ammonium fresh and free from

polysulphide. A more satisfactory plan is to saturate the solution of nickel with sulphuretted hydrogen, and then to add ammonia to slight alkaline reaction. The precipitate is then filtered off as rapidly as possible, and washed with dilute sulphuretted hydrogen water. If this precipitation is for quantitative purposes, it must be remembered that when the sulphide of nickel is ignited, some of the sulphur goes off, whilst another part oxidises and remains as sulphate of nickel, the result being a variable mixture of disulphide, sulphate, and oxide of nickel. Forbes has examined this reaction and has based upon it an ingenious plan for estimating nickel. As the equivalent of the sulphur in the sulphide of nickel, and of the oxygen in the oxide are identical, the sulphide and the oxide will be of the same weight, and this fact enables us at once to calculate the amount of nickel contained in a mixture of the disulphide and oxide, however variable the relative proportions of these compounds may be, and it becomes only necessary to remove the small amounts of sulphuric acid present in the incinerated sulphide in order to determine the amount of nickel present. The addition of a small amount of pulverised carbonate of ammonium to the incinerated sulphide as soon as it is cold, and then carefully heating until all ammoniacal salts are expelled, completely effects this object. In estimating the nickel present the calculation may be made as if the calcined mass were either all disulphide or all oxide.

It will be found most convenient to add the carbonate of ammonium to the incinerated sulphide in the same crucible in which it has been ignited, or rather to cover the ignited sulphide with four or five times its volume of this salt, and then, by means of a small agate pestle or glass rod, to break up all grains and mix it well together by trituration; this can easily be effected without any loss whatever, as the superstratum of carbonate of ammonium effectually prevents any particles flying over the sides of the crucible. This, with its cover loosely placed upon it, is now very gently heated until nearly all ammoniacal salts are expelled: then the heat is increased for an instant, and the whole, after cooling over sulphuric acid, is weighed and estimated as usual.

Nickel may be very accurately determined by Leison's oxalic acid process, for details of which see Zinc, p. 63. In the case of sulphate of nickel it is necessary, after adding the oxalic acid, to concentrate the mixture on a water-bath before adding alcohol, and then further to digest for about half an hour, replacing the alcohol as fast as it evaporates. The oxalate is collected on a paper filter, and after washing, dissolved in ammonia on the filter. The filtrate is then acidified with sulphuric acid, when it is ready for titration with permanganate of potassium. But the solution containing sulphate of nickel has a green colour, which would interfere with the delicacy of the permanganate test, and to overcome this difficulty an

ingenious artifice may be adopted, first employed, we believe, by Dr. W. Gibbs, and based on an observation of Maumené. The colours of cobalt and nickel are exactly complementary one to the other, so it is only necessary to add gradually a solution of sulphate of cobalt to the green nickel solution, when the colour of the latter is gradually discharged, finally giving place to a neutral tint, which in no way interferes with the delicacy of the permanganate colour test. Although the object is to ascertain the amount of nickel present, this is really effected by estimating the quantity of oxalic acid which was united with it, therefore the addition of cobalt at this stage of the process does not interfere.

Separation of Nickel from other Metals.

The description of the separation of nickel from the metals which have been already referred to will, for convenience, be postponed until the corresponding separations of cobalt are discussed, when they will both be treated of together.

COBALT.

Metallic Cobalt.

Metallic cobalt is precipitated from the aqueous solutions of its salts by magnesium in exactly the same manner as metallic nickel. The subsequent treatment is identical. After fusion in a lime crucible cobalt is one of the most tenacious of known metals, and when made into wire it supports almost double the weight which would break an iron wire of the same thickness.

Estimation of Cobalt.

Leison's process with oxalic acid and permanganate is equally successful with cobalt as with nickel (p. 148)—a few modifications are necessary. The solution is precipitated in the usual way by oxalic acid and alcohol, but it is then collected on a sand-filter and digested with dilute sulphuric acid. The solution, which will be very red, must then be mixed with a solution of sulphate of nickel until the red colour disappears and a faint smoky hue takes its place; the subsequent titration is performed in the customary manner.

Cobalt cannot be estimated by precipitation as sulphide and calcination with subsequent addition of carbonate of ammonium, in the way described under Nickel. Mr. Forbes, who has experimented on this method, says that the calcined mass, instead of consisting of a mixture of oxide and disulphide of cobalt, is quite pink from the presence of sulphate of cobalt, which appears most strongly to resist decomposition.

Tests for Cobalt.

If to a solution of a salt of cobalt in tartaric or citric acid an excess of ammonia is added, the addition of ferricyanide of potassium will cause a

very dark red colouration in the solution. Mr. Skey says that the colour thus produced by the ferricyanide is so intense that it will reveal the presence of cobalt in solution when all other tests fail, its delicacy being about four times greater than that of carbonate of ammonium. A solution of cobalt prepared as indicated above, so as only to contain $\frac{1}{20000}$ part of cobalt, when placed in a $\frac{3}{8}$ inch test-tube, is very distinctly coloured by the addition of a soluble ferricyanide, and even when diluted down so as to contain but one part of cobalt in 400,000 parts of the liquid, the colouration is still distinctly visible in a bulk of a few ounces.

Another very delicate test is given by Herr Schönn. If a drop of cobalt solution be added to a concentrated solution of sulphocyanide of sodium, a blue mass is the result. This mass is composed, either immediately or after evaporation, of acicular blue crystals, probably of sulphocyanide of cobalt, which are easily soluble in water and alcohol, but insoluble in disulphide of carbon. This reaction may be used as a test for cobalt. A drop of a solution containing 0·0005 part of cobalt produces, with sulphocyanide of sodium, only a green colour, at ordinary temperatures; on heating, however, the mass becomes blue. As the cobalt solution should always be concentrated, it is well to evaporate dilute solutions nearly to dryness, then add the reagent, and heat. According to Schönn, neither iron, zinc, manganese, nor nickel interferes with the reaction, provided the solution be perfectly neutral.

Separation of Cobalt and Nickel.

The following is a convenient method of detecting cobalt and nickel in ordinary analysis, although the process is not sufficiently accurate for quantitative purposes:—To the slightly acid solution containing the two metals, first an excess of chloride of ammonium is added; this causes the ferricyanide of cobalt afterwards formed, which otherwise would run through the filter, to fall in a denser state, and also of much darker colour, often nearly black. Ferricyanide of potassium is then added, until the precipitation is complete, and it is afterwards strongly agitated with a considerable excess of ammonia. Upon filtering, the cobalt remains upon the filter, being recognised by the characteristic colour of the precipitate, and the nickel is readily detected in the filtrate by means of sulphide of ammonium.

A method of separating nickel and cobalt, given some years since by Liebig, consists in boiling the mixed double cyanides of nickel and potassium and cobalt and potassium with oxide of mercury. Oxide of nickel is precipitated, while an equivalent quantity of mercury is dissolved in the cyanide. The method certainly gives good results, but is not free from objection. Long boiling is necessary before the precipitation is complete, and it is difficult to prevent bumping during ebullition. The excess of oxide of

mercury must be separated from the oxide of nickel by a special operation, and the nickel afterwards again precipitated by caustic alkali.

These inconveniences may be completely avoided, according to Wolcott Gibbs, by employing, instead of the oxide alone, a solution of the oxide in the cyanide of mercury. When this solution is added to a hot solution of the double cyanide of nickel and potassium, the whole of the nickel is immediately thrown down as a pale green hydrate of the protoxide. Under the same circumstances, cobalt is not precipitated from the double cyanide of cobalt and potassium. Mr. W. N. Hill, who has repeatedly employed this method and carefully tested it, has found that the separation effected is complete. No cobalt can be detected in the precipitated oxide of nickel by the blowpipe, nor can the nickel be detected in the cobalt (finally separated as oxide) by Plattner's process with the gold bead. The solution of oxide of mercury is easily obtained by boiling the oxide with a strong solution of the cyanide, and filtering. The hydrated oxide of nickel precipitated may be filtered off, washed, dried, ignited, and weighed. The cobalt is more readily and conveniently determined by difference when the two metals have been weighed together as sulphates.

Mr. T. H. Henry has mentioned another objection to Liebig's process referred to above. The cyanide of potassium employed should be free from cyanate, and as the commercial salt always contains cyanate Liebig proposed instead the employment of hydrocyanic acid and caustic potash. Mr. Henry fuses commercial cyanide of potassium, for a few minutes, with a little pure charcoal, and, when cold, dissolves it in water and uses this solution instead of the pure salt or the mixture of hydrocyanic and potash. The rest of the operation may be carried out as directed by Liebig (boiling the solution with oxide of mercury), or by Dr. Gibbs's modification, as described in the preceding paragraph. Mr. Henry says that he believes this process to be one of the most elegant, accurate, and expeditious in the whole range of analytical chemistry.

M. A. Terreil has founded a method of separating nickel and cobalt on the insolubility of chloride of roseo-cobalt in acid liquids and ammoniacal salts, and on the rapid transformation of ordinary salts of cobalt into salts of roseo-cobalt under the double influence of ammonia and oxidising bodies —such as permanganate of potassium and alkaline hypochlorites.

The process is carried out in the following manner:—To the solution of the two metals add an excess of ammonia, so as to re-dissolve the two oxides; add to the hot ammoniacal liquid a solution of permanganate of potassium, sufficient to cause the liquid to remain coloured violet for a few instants by the excess of permanganate. Boil the liquid for a few minutes, then add a slight excess of hydrochloric acid, to re-dissolve the oxide of manganese which will have formed. Heat the liquid gently for 20 or

25 minutes, then let it stand for about 24 hours. At the end of that time all the cobalt will be deposited in the form of a beautiful red-violet crystalline powder; the precipitate is chloride of roseo-cobalt, which collect on a weighed filter; wash it on the filter first with cold water, then with dilute hydrochloric acid, or with a solution of sal-ammoniac, and then with ordinary alcohol, which frees it from sal-ammoniac. Dry it at 110° C., and weigh. 100 parts of chloride of roseo-cobalt correspond to 22·761 of metallic cobalt. It is, however, better to take a given quantity of the roseo-cobalt salt, and reduce it by dry hydrogen; this leaves perfectly pure cobalt to be weighed.

Next boil the solution containing nickel to expel the alcohol which has been introduced in washing the cobalt salt; saturate it with ammonia, add another small excess of permanganate of potassium, and boil. All the manganese will be precipitated; filter the liquid, and all the nickel will be found in the filtrate, from which it may be easily separated in the state of sulphide, and then transformed into oxide. By this process the presence of a ten-thousandth part of cobalt in a salt of nickel may be ascertained.

In this operation an alkaline hypochlorite may take the place of the permanganate of potassium, but then the deposit of roseo-cobaltic salt takes place with extreme slowness, and several days are required to complete it. This reagent is preferable to permanganate when manganese is to be separated from nickel and cobalt.

The nitrite of potassium process of separating nickel and cobalt is very accurate in experienced hands, although it is liable to fail with beginners. Moreover, the complete precipitation of the cobalt is rarely complete under forty-eight hours. It is best effected as follows:—Concentrate the mixed solution of cobalt and nickel as much as possible, nearly neutralise with potash, add a saturated solution of nitrite of potassium and a little acetic acid. Allow the liquid to rest for from 24 to 48 hours. The yellow precipitate of double nitrite of cobalt and potassium is then filtered off, washed with a solution of chloride of potassium, and afterwards dissolved in hydrochloric acid, and precipitated a second time in the form of oxide of cobalt by the addition of caustic potash. The filtrate from the double nitrite contains all the nickel, which may also be precipitated as oxide by the addition of caustic potash.

Separation of Nickel and Cobalt from their Ores and from one another.

As the constituents of a cobalt or nickel ore may be of the most varied description, it is necessary, before attempting to effect a complete separation and estimation of these two metals, either to begin with a careful qualitative analysis, and then to select methods for the separation of each foreign

constituent, which would often involve a number of distinct troublesome processes not fitting conveniently one into the other, or else to be in possession of a method so generally applicable as to be capable of effectually eliminating nickel and cobalt from all other elements; and at the same time so simple that even if certain elements, which it is especially designed to separate, should happen not to be present, it would cause no unnecessary waste of time. Mr. E. Ash Hadow has devised an analytical process which is generally applicable to all descriptions of ores of these metals, and he has also suggested a method by which the cobalt constantly contained in the ores of manganese may easily and profitably be rescued from the waste manganese solutions of the bleaching powder works.

The following is condensed from Mr. Hadow's original paper, which will be found in the "Chemical News," vol. ii., p. 85:—If no qualitative analysis of the ore has been previously made, we must presume, in the quantitative separation of cobalt and nickel, that all other common elements are present; attention, however, need only be specially given to those elements, or their compounds, of which the separation is particularly difficult; these are iron, manganese, zinc, aluminium, magnesium, calcium, soluble silica, arsenic and phosphoric acids. By employing, however, the method usually applied to the separation of phosphoric acid for the removal of iron, arsenic, and aluminium, and one of the methods recommended for the separation of manganese from cobalt, for the removal likewise of magnesium, calcium, soluble silica, and the last traces of aluminium, and by a slight modification for the detection and separation of zinc, the analysis becomes short, easy, and accurate.

The only examination which the ore need undergo previously to the solution of a weighed quantity, is with the view of obtaining a rough idea as to the amount of arsenic and cobalt or nickel present in the sample; for this purpose a little may be roasted on charcoal, or ignited in a tube, to see whether arsenic readily sublimes; another portion, of a few grains weight, may be dissolved in aqua regia in a test-tube, when the depth of the blue or green colour will serve as an indication of the degree of richness of the ore in cobalt and nickel.

If the ore is rich, from 20 to 30 grains; if poor, from 50 to 100 grains, in a state of fine division, are weighed out for the analysis. If much arsenic has been found, the portion, after weighing, had better be ignited in a small porcelain capsule or crucible over a gauze burner, when it generally ignites and smoulders away, evolving abundance of arsenious acid. The powder ready for solution is transferred to a small 4-oz. flask by means of glazed letter paper and a camel's-hair paint brush to sweep in the last particles; the mouth of the flask is then partially closed by a small funnel placed to catch the drops projected during solution. The ore is then drenched with

hydrochloric acid, nitric acid being added from time to time, until all heavy metallic-looking particles are found to have disappeared from the bottom of the flask. The solution may then be decanted from the insoluble matters into a half-pint beaker, together with the washings of the flask; and as sulphur frequently remains, entangling portions of undissolved ore, it is advisable to transfer the undissolved residue from the flask into a capsule, drying and igniting the contents of the latter, and then digesting again the ignited matters in a little more aqua regia; the whole of the latter, both dissolved and undissolved, may now be added to the first portion in the half-pint beaker.

To separate out iron, arsenic, phosphoric acid, and aluminium from the solution, acetate of sodium may be added at once, and the liquid boiled; a far better mode, however, is to effect a *partial* separation of these ingredients by the addition of carbonate of calcium in excess to the solution of the ore, and after filtering out the solution containing the greater portion of the cobalt and nickel, and partly washing the precipitate, to extract the last traces of cobalt and nickel from the latter by dissolving it in hydrochloric acid, adding excess of acetate of sodium, and boiling. The first filtrate from the precipitate by carbonate of calcium had better be collected apart from the second filtrate from the precipitate produced by acetate of sodium, and received in a beaker capable of holding at least a quart. The solution of the precipitate by carbonate of calcium is best effected in a beaker, after the removal of the precipitate from the filter; this is easily effected by inclining the funnel over the beaker and sending a stream of water from the wash-bottle between the filter and the upper edge of the mass of precipitate, when the latter will soon become detached and slide off into the beaker below; it is here treated with dilute hydrochloric acid, to dissolve all but the insoluble residues of the ore which had not been previously filtered off, and then a solution of acetate of sodium is added in excess (indicated by the deep red colour of liquid), and the whole, heated to boiling, may be filtered at once. Iron thus separated out, in presence of free acetic acid, has less tendency to retain cobalt than when precipitated by means of carbonate of calcium, besides which the cobalt and nickel in the filtrate are left in the condition of acetates, a necessary step preparatory to their separation from manganese, &c.

This method of separating out iron, &c., though very effectual, was often at first found to be attended with difficulties, for if much arsenic were not present the basic acetate of iron frequently became slimy towards the end of the filtration, only allowing the boiling washing water to pass with such extreme slowness as to render the method almost useless, until it was found that the addition of a little sulphate of sodium during the washing at once and permanently effected a cure, causing filtration to proceed rapidly,

and diminishing the tendency of the iron to pass the filter; another difficulty was, that when acetate of sodium was added at once to the original solution of the ore, the solution, often containing much cobalt and nickel as acetates, and filtered in a concentrated state, yielded to the filter paper sufficient cobalt and nickel to occasion distinct loss; this was avoided by separating out the great bulk of the cobalt and nickel in solution as chlorides by means of carbonate of calcium, as above recommended, and then the weaker solution, being comparatively strongly acid, could be filtered without loss. This second filtrate may still retain traces of iron; a little acetate of sodium may be added to make sure that none remains in the condition of chloride, which would be indicated at once by a reddening of the liquid, and the whole is then boiled thoroughly once more, if rendered at all turbid passed through a filter again, then nearly neutralised with ammonia, and finally added to the bulk of the cobalt and nickel solution in the quart beaker. There will in all probability be enough of the acetates of sodium and ammonium present to convert the entire quantity of cobalt and nickel into acetates without further addition, and rendering it thus ready for the next operation.

If sulphuretted hydrogen be now transmitted through the solution containing cobalt and nickel, these metals are perfectly and completely separated without a trace of manganese, magnesium, calcium, aluminium, or soluble silica, which, when present, invariably accompany the sulphides precipitated by sulphide of ammonium; the sulphides, moreover, thus precipitated from an acetic solution, have much less tendency to oxidise while on the filter, so that their washing may be more perfectly accomplished than in the former case. The passage of sulphuretted hydrogen may be conveniently effected at the end of the day, and the next morning the sulphides will be found perfectly settled at the bottom of the beaker, permitting the great bulk of the liquid (tested first to make sure of the removal of cobalt and nickel) to be drawn off and thrown away, or at least rapidly run through a filter; the sulphides collected at the bottom, together with that which always adheres to the sides of the beaker, and which may be detached without loss by a caoutchouc-covered glass rod, are then well washed on the filter with boiling water until all soluble matters are perfectly removed. The sulphides, perfectly washed, are now to be dried by placing the funnel with the filter in a broken beaker on wire gauze, at a safe distance over a lamp, and when dry they may be detached from the filter into a small beaker of from 1 to 2 oz. capacity, capable of being covered with a watch-glass; the filter itself is ignited, and the well burnt ashes added to the sulphides, which are then to be *cautiously* treated with nitric acid, the action being rather violent, and, if care be not taken, liable to occasion loss. With the aid of a little heat the whole should pass into solution.

In addition to cobalt and nickel the solution may still contain zinc,

together with copper, and other metals precipitable by sulphuretted hydrogen from hydrochloric solutions; by passing sulphuretted hydrogen now through the nitric solution, somewhat diluted, these latter are readily precipitated and removed by filtration. Zinc, however, may still remain, to detect and remove which it is necessary to expel the sulphuretted hydrogen still remaining in the solution by boiling, to add solution of ammonia until a precipitate occurs, and then to acidify pretty strongly with acetic acid; if sulphuretted hydrogen slowly transmitted, or fresh sulphuretted hydrogen water, occasions a milkiness, zinc is present, and the slow passage of the gas is to be continued until the precipitate begins to show signs of darkening. The liquid is then filtered. The zinc may be identified as such by collecting and igniting the precipitate, when a trace of cobalt carried down with it (and which may be separated out, if desired, by a repetition of the process on the precipitate) will produce the beautiful and well known Rinman's green.

The filtrate, containing only nickel, cobalt, and salts of ammonium, is treated with some pure sulphuric acid and evaporated to dryness in a weighed capsule, and heated sufficiently to expel the excess of sulphuric acid and all the ammoniacal salts. The residual sulphates of cobalt and nickel may now be weighed in a covered crucible. This form of weighing these metals is easy, exact, and may be rapidly executed. The weight of the ash of a filter of the size used for collecting the sulphides must be ascertained after treatment with sulphuric acid, and subsequent expulsion of the excess, and this weight deducted from the total sulphates, in order to obtain perfectly correct results.

If it be desired to weigh these metals as oxides, pure potash or carbonate of sodium must be substituted for ammonia, with acetic acid, for the removal of zinc, and after the precipitation of the latter the filtrate must be first acidified with hydrochloric acid and boiled to expel sulphuretted hydrogen, and finally supersaturated with potash; the precipitate thus obtained is, however, difficult to wash, and almost always contains some silica derived from the potash or the vessel in which the operation was conducted, and is not to be recommended as so convenient or exact a form as that of the sulphate. After ignition of the oxides, the nickel exists as NiO, and the cobalt as Co_3O_4.

Binoxalate of potassium serves as a perfect precipitant of nickel, but cobalt is not so thoroughly separated; the first goes down as a double salt of nickel and potassium, the latter as a simple oxalate; both precipitates are very easily washed, and give perfectly correct results with nickel, nearly correct with cobalt; the former precipitate must, after ignition in an open crucible, be washed with a little water to remove the carbonate of potassium, and again dried and weighed as oxide, NiO; the oxalate of cobalt strongly ignited in the open air leaves the oxide Co_3O_4.

It now only remains to separate the nickel and cobalt from each other. If the colour of the solution indicates that the latter is in excess, Liebig's method of separation by converting the metals into double cyanides is probably preferable to any other; perfectly correct results are, however, only attained when certain precautions are taken; in the first place, it is not altogether a matter of indifference whether the mixed sulphates or the oxides brought into solution in hydrochloric acid be treated with potash or with hydrocyanic acid first, unless, indeed, the potash be perfectly free from silica; if the latter be present, and the potash is added first, the precipitate produced frequently refuses wholly to dissolve on the addition of hydrocyanic acid, and though liable to be disregarded from making little show in the coloured liquid, it will, if filtered off, be found to retain cobalt. Therefore, hydrocyanic acid should always be added first, and the subsequent addition of potash will then produce perfect solution, even though silica should be abundantly present in the potash; a condition which is, however, to be avoided, as the silica will afterwards attach itself to the nickel precipitate. The most important point to be attended to is the complete conversion of the cobaltous- into the cobalti-cyanide, a change which is effected by the absorption of oxygen from the air, which takes place with great rapidity; but still not so rapidly but that, by the hasty addition of oxide of mercury, a considerable quantity of cobalt might be precipitated with the nickel. The change from the absorption of oxygen is easily seen if the solution is cold, by the liquid, at first of a deep yellowish-green, becoming rapidly, from the surface downwards, of a deep reddish-brown, which changes to pale yellow when warmed. There is no need of *free* hydrocyanic acid, neither can any hydrogen be observed to escape on boiling the solution of a cobaltous-cyanide. When the change from cobaltous- into cobalti-cyanide is complete (which may be ascertained by withdrawing the source of heat and observing whether the cooling liquid continues to remain of a pale yellow colour) the nickel may be precipitated either as pale hydrated protoxide, by the addition of precipitated oxide of mercury, or as the black hydrated sesquioxide, by means of chlorine or chloride of soda.

The latter appears to be the best of the two methods, for the following reasons:—1st. That it serves as a qualitative test in the first instance for the presence of nickel, the *least trace* of the sesquioxide giving an inkiness to the liquid, whereas, when oxide of mercury is used, the excess of oxide of mercury completely disguises a small quantity of the pale green protoxide of nickel, which can only be detected after washing and igniting the precipitate. 2nd. The hydrated protoxide separated by oxide of mercury may easily carry down some cobalt as cobalti-cyanide of nickel unless the liquid is strongly alkaline, which is not the case with the sesquioxide, even when precipitated from liquids nearly neutral. 3rd. The first action of the chlorine,

or chloride of soda, is upon the cobaltous-cyanide, effectually ensuring its conversion into cobalti-cyanide, before the cyanide of nickel is touched. 4th. The sesquioxide of nickel is washed with far greater ease and rapidity than the protoxide. If potash is used it must be pure and free from silica and aluminium, hence, for the sake of economy, carbonate of sodium may be substituted for it, the carbonic acid escaping with effervescence on the passage of chlorine into the boiling liquid. A more convenient way, perhaps, is to add to the boiling solution of the cyanides a previously prepared solution of chloride of soda containing excess of carbonate of sodium, as long as it continues to produce a precipitate.

If the separation of nickel by oxide of mercury be preferred, a solution of a salt of mercury may be substituted for the previously prepared oxide with advantage as regards economy, rapidity, and neatness; the excess of alkali in the liquid produces a momentary precipitation of oxide of mercury with each drop added, until the nickelous-cyanide has been wholly decomposed, when the yellow colour of the oxide of mercury appears permanently.

If it be desired to weigh the cobalt of the cobalti-cyanide, after the separation of the nickel by Wöhler's method of precipitating the solution with nitrate of the suboxide of mercury, chlorides and sulphates are to be avoided as giving rise to very bulky precipitates; and accordingly, after the separation of zinc, the nickel and cobalt should be precipitated by potash, brought into solution in nitric acid, and after conversion into cyanides, nitrate of protoxide of mercury may be used to separate out nickel. In washing the cobalti-cyanide of the suboxide of mercury, its disagreeable tendency to pass through the filter towards the conclusion of the washing may be effectually prevented by adding a little nitrate of suboxide of mercury to the washing water.

If the colour of the solution of the mixed oxides indicates that nickel is decidedly in excess, it will be better before proceeding to separate out the cobalt by Liebig's method, to concentrate the cobalt by a previous partial separation by a method which Mr. Merry, of Swansea, employs to effect a complete and entire separation of the two metals. It is a modification of Rose's method for their separation, and consists in adding to the perfectly neutral solutions of the two, a solution of chloride of lime as long as it produces an immediate black precipitate of sesquioxide of cobalt. To extract the last traces of cobalt the addition of chloride of lime must be carried somewhat beyond this, since a black precipitate forming even after some minutes often contains a trace of cobalt; if there be much of the latter the liquid must be neutralised from time to time with lime-water or milk of lime. The black precipitate, containing all the cobalt with some nickel, can then be brought into solution, and the cobalt separated out either by Liebig's method or by a repetition of the above process.

This method is a very useful one for detecting the *smallest trace* of cobalt in a solution of nickel:—The solution digested in the cold on carbonate of lime, to render it neutral, is filtered and treated with a few drops of a solution of chloride of lime; if cobalt is present to a certain extent an immediate brown cloud is perceived, but if far less than this the dark precipitate which will form after some time will certainly contain cobalt, if any be present, and on dissolving in borax will become manifest; if not at once, at least when the nickel has been reduced by ignition on charcoal before the blowpipe, by the blue colour of the bead.

The property which cobalt possesses of being perfectly precipitated from its acetic solution by sulphuretted hydrogen, and thus of being separated from manganese, might probably be profitably employed to rescue the cobalt which is contained in the solutions of manganese from the bleaching-powder works. All that is necessary is to add to the liquid an excess of chalk, which would remove all the iron and render the liquid neutral; the latter drawn off from the precipitate would merely require the addition of a very little acetate of sodium, about 90 parts of the dried salt to every 40 of the commercial oxide of cobalt in the liquid (which would have to be determined by a separate examination of a portion), and then sulphuretted hydrogen transmitted would precipitate all the cobalt as sulphide at once.

Extraction of Nickel from its Ores.

The ore of nickel usually met with is the arsenide, containing variable quantities of cobalt and iron, and frequently also copper and bismuth. It is finely powdered, mixed with 2 parts of solid caustic soda and 1½ parts of sulphur, and fused in an earthen crucible, gradually increasing the heat to dull redness, at which temperature it is to be kept for some time. The mass is then digested in water, which dissolves the soluble sulpho-arseniate of sodium, and leaves, when washed by decantation, crystallised sulphide of nickel. Attack this with warm hydrochloric acid containing a little nitric acid.

The solution heated to about 70° C. is then submitted to a current of sulphuretted hydrogen, which must be continually passed until the liquid is cold. It is then to be covered over and left at rest for 24 hours; the arsenic, copper, and bismuth come down as sulphides. These are filtered off, and the filtrate is heated with chlorate of potassium or hypochlorite of sodium, to bring the iron to the state of sesquioxide, which is then precipitated by ebullition with excess of acetate of sodium. The filtrate from the basic acetate of iron is concentrated by evaporation and mixed with a saturated solution of nitrite of potassium,* which will precipitate all the cobalt.

* Nitrite of potassium is prepared by fusing, in an iron crucible, 1 part of nitre with 2 parts of granulated lead, stirring well with an iron spatula, and then heating to redness until the lead is completely oxidised. The fused mass, after cooling, is extracted with water, and the small amount of lead which is dissolved is precipitated by carefully adding a mixture of caustic ammonia and carbonate or sulphide of ammonium.

The yellow precipitate washed with a saturated solution of chloride of potassium may be treated as described below. The nickel is precipitated from the liquid either in the state of oxide by means of caustic potash, or after concentration, by a saturated and warm solution of binoxalate of potassium. The precipitated oxalate upon calcination leaves pure nickel.

Purification of the Metallic Nickel of Commerce.

Dissolve the metal in hydrochloric acid containing a little nitric acid. Pass sulphuretted hydrogen through the solution until the metallic impurities are thrown down, and then precipitate the nickel and cobalt by a warm saturated solution of binoxalate of potassium. The precipitate after being washed and calcined leaves the nickel (containing a little cobalt) in the metallic state. Dissolve again in hydrochloric acid containing a little nitric acid, and separate by means of nitrite of potassium.

Preparation of Metallic Cobalt from its Ores.

Metallic cobalt may be prepared from its ores (arsenide or sulphide) by a similar process to that adopted in the case of nickel (p. 159). When the mineral contains more than 70 per cent of arsenic, a preliminary fusion should be performed with chloride of sodium, to remove most of the arsenic. This may be continued by roasting or by fusion with a mixture of carbonate of sodium and sulphur.

As nickel is almost invariably present in cobalt ores, this metal will require to be separated. Wöhler recommends for this purpose the nitrite of potassium process (see p. 152). The yellow cobalt precipitate is dissolved in as small a quantity of hydrochloric acid as possible, and acetate of sodium is then added; the addition of a warm saturated solution of oxalic acid now precipitates the cobalt as oxalate. This oxalate after being washed and dried may be packed closely in a crucible of biscuit porcelain, protected by enclosure in a Hessian crucible. The covers being well luted on, the whole is heated in a wind furnace or a forge. If a sufficient temperature has been obtained the cobalt will be in the form of a fused button.

Separation of Nickel and Cobalt from Manganese.

The separation of nickel and cobalt from manganese may be effected by Terreil's process (see p. 151).

Manganese may be detected when in the presence of a very large excess of cobalt or nickel by means of Crum's test with Dr. Gibbs's modification (p. 149). The solution of cobalt which is suspected to contain manganese is first to be freed as completely as possible from arsenic, copper, and iron. To a portion of this solution contained in a test-tube a solution of a pure

salt of nickel is to be gradually added, until the colour of the mixed fluid vanishes or becomes almost insensible. Nitric acid and peroxide of lead are then to be added and the whole boiled for a few seconds, when the characteristic tint of a permanganate will appear, if but a trace of manganese be present. The same process is to be applied in testing solutions of nickel for small quantities of manganese, a pure solution of cobalt being added till the original green colour of the solution is destroyed. It rarely happens in the application of this method that a perfectly colourless solution can be obtained; usually, the mixed solution has a faint brown tinge, like that of commercial sulphuric acid. This tint, however, has no sensible influence on the result.

In all cases where this test is employed the colour of the liquid must be observed immediately after boiling and subsidence of the excess of peroxide of lead, as the tint fades when the solution is exposed to air and light.

Dr. Wolcott Gibbs, to whom analytical chemistry is so greatly indebted, effects the separation of manganese from nickel and cobalt (and zinc also if present) in the following way:—To the neutral or nearly neutral solution of the chlorides, acetate of sodium is to be added in excess, together with a few drops of free acetic acid. The solution is then to be boiled, and a rapid current of sulphuretted hydrogen passed through it while boiling, and continued for half an hour. Every trace of cobalt, nickel, or zinc is precipitated in the form of sulphide, while the whole of the manganese remains in solution. The precipitate is to be thrown on a ribbed filter and quickly washed with cold water saturated with sulphuretted hydrogen. It is easily washed, and though the sulphides of cobalt and nickel precipitated in this manner are far more easily oxidised than when precipitated by boiling sulphide of sodium from boiling solutions, they will be found to present no difficulty as regards oxidation upon the filter. Manganese may then be determined in the filtrate by boiling with hydrochloric acid and precipitating in the usual manner with carbonate of sodium. The mixed sulphides upon the filter—supposing for the sake of generality that all three are present—are to be dissolved in hydrochloric acid, and the metals converted into double cyanides by means of an excess of cyanide of potassium, after which the zinc may be precipitated by means of sulphide of sodium, as recommended by Wöhler.

When perfectly pure cyanide of potassium is not at hand, the following process will be found particularly convenient:—Acetate of sodium is to be added to the solution of the mixed chlorides, after which the vapour of hydrocyanic acid, generated in a flask from sulphuric acid and ferrocyanide of potassium, is to be passed directly into the solution. Cyanide of zinc is immediately precipitated more or less completely as a perfectly white powder. A solution of sulphide of sodium is then to be added as long as a

precipitate is formed, after which the sulphide of zinc is to be separated by filtration. Cobalt and nickel remain in solution as double cyanides. The same process may be used to separate manganese from cobalt and nickel, sulphide of sodium throwing down under these circumstances a pure flesh-red precipitate. It is easy to see that zinc and manganese together may be separated from cobalt and nickel by the same process and at one operation. No cyanide of manganese appears to be formed when hydrocyanic acid is passed into a solution containing a salt of manganese, acetic acid, and acetate of sodium.

The sulphides of nickel and cobalt are thrown down from boiling solutions by a boiling solution of sulphide of sodium in an insoluble form, so that, in fact, even strong hydrochloric acid scarcely exerts upon them an appreciable action. This process has been applied to the separation of cobalt and nickel from zinc and manganese by Mr. Perkins, and gives results which are very satisfactory, especially for qualitative purposes; the sulphides of manganese and zinc precipitated under the same circumstances being readily soluble, even in dilute acid.

Separation of Nickel and Cobalt from Iron.

F. Field separates nickel and cobalt from peroxide of iron by precipitating the latter with oxide of lead. In the case of nickel and iron, the nitrates are evaporated nearly to dryness, and after the addition of water, oxide of lead (litharge) is added, and the whole boiled for ten minutes or a quarter of an hour. The iron is entirely precipitated, the nitrates of nickel and lead remaining in solution. After filtration, which can be effected with great readiness, dilute sulphuric acid is added, and on standing for sixteen hours the sulphate of lead is filtered off, and the nickel precipitated and estimated in the usual manner. The filter containing the peroxide and excess of litharge is digested in dilute sulphuric acid, filtered, and washed. The filtrate is precipitated by potash.

It may here be remarked that oxide of nickel can be more readily determined by precipitation as peroxide by means of hypochlorite of sodium than as oxide by caustic potash. Peroxide of nickel, after boiling the solution in which it is suspended, separates as a rather dense precipitate, and can be easily washed, whilst the great difficulty of freeing the potash from the bulky gelatinous protoxide is well known. The alkali, indeed, adheres with remarkable pertinacity to this substance, and if not added with considerable caution, and other circumstances attended to, very protracted washing is necessary. In employing the hypochlorite of sodium, it is requisite to have an open vessel, a beaker for instance, as the peroxide is liable to form flakes upon the sides of the glass, which are difficult to remove from a narrow-necked flask. The peroxide is heated to whiteness, and the nickel weighed as protoxide.

Cobalt can be separated from iron in precisely the same manner as nickel. Many analyses have shown that no trace of cobalt is precipitated from its solution on boiling with oxide of lead, and even when the iron is in considerable excess, 50 to 1 for example, the separation is complete. The solution of cobalt freed in this manner from iron contains no trace of that metal, gives no shade of blue with ferrocyanide of potassium, nor can iron be recognised by any known test.

Wöhler separates nickel and cobalt from peroxide of iron by adding a large quantity of chloride of ammonium and then excess of ammonia. The sesquioxide of iron is precipitated, whilst the nickel and cobalt remain in solution. Slight traces of the latter metals are, however, carried down by the iron.

Sesquioxide of iron may be perfectly separated from cobalt and nickel by boiling the neutral or nearly neutral solutions with acetate of sodium, provided that the following precautions are observed:—The solutions from which the iron is to be precipitated must be dilute; half a litre of the solution should not contain more than one grain of the sesquioxide. The quantity of acetate of sodium should be sufficient to convert by double decomposition all the bases present into neutral acetates. The acetate should be added to the metallic solution when cold, and the whole should then be heated together and boiled for a short time. It is not necessary to filter upon a water-bath funnel, but the beaker containing the solution should be kept nearly at the boiling point during filtration, and a ribbed filter should be employed. It is especially necessary where nickel is present to add a few drops of free acetic acid to the solution, to prevent the formation of basic acetates of the protoxides. Finally, it is best, whenever possible, to have all the bases present in the form of chlorides. The iron upon the filter in the form of basic acetate must, whenever an absolutely complete separation is necessary, be re-dissolved in hydrochloric acid, and again be precipitated by boiling with the acetate after rendering the solutions nearly neutral by means of carbonate of sodium. In this manner only it is possible to separate the last traces of the stronger bases. Finally, the basic salt of iron, after washing, must be re-dissolved in hydrochloric acid, and precipitated by boiling with ammonia in the usual manner, to free it completely from alkali.

Separation of Nickel or Cobalt from Zinc.

M. Brunner gives the following solution of this problem:—The solution of the two metals (zinc and nickel, or zinc and cobalt) in hydrochloric or nitric acid, is diluted with a large quantity of water, and almost completely neutralised by carbonate of sodium. To effect this, a slight excess of the latter is added, and the precipitate which ensues is re-dissolved in a few

drops of acid, so as to introduce a very slight excess of the latter. A current of sulphuretted hydrogen is then made to pass through the liquid, and to complete the precipitation of the zinc, a few drops of a diluted solution of acetate of sodium are added to the liquid. Care must be taken not to introduce an excess of acetate, and not to heat the liquid. A fresh current of sulphuretted hydrogen is now allowed to pass, until the precipitate does not appear to increase. The vessel is then left to itself for ten or twelve hours at the ordinary temperature, after which the precipitate is collected in a filter and washed. To make sure that all the zinc has been thrown down, a drop of acetate of sodium may be added to a little of the filtered liquid, which should remain clear when a little sulphuretted hydrogen is introduced. The nickel or cobalt is thrown down from the filtrate by potash. If the original solution contain iron, it is essential to separate it first of all by carbonate of barium.

A very good plan for separating nickel from zinc is given by Wöhler as an illustration of the method of analysing German silver (an alloy of nickel, zinc, and copper):—The copper having been separated from the other metals (see Copper), the liquid, after being filtered and reduced, by evaporation, to a small bulk, is treated by excess of caustic potash, and then by hydrocyanic acid, until the precipitate which is at first formed is completely redissolved with a yellow colour. In this liquid, which contains double cyanides, the zinc is precipitated in the state of sulphide, by means of protosulphide of potassium (not sulphide of ammonium). After some hours' digestion, and when the precipitate is completely deposited, it is filtered off, and, after boiling the liquid with aqua regia, the nickel is precipitated as oxide by caustic potash. This oxide must be calcined after it is dried.

Separation of Nickel or Cobalt from Uranium.

Dr. Gibbs's method already given for the separation of manganese from cobalt, zinc, and nickel, by precipitating the sulphide of the three last-named metals by means of sulphuretted hydrogen from a boiling solution of the acetates (p. 161), may be also used for the separation of uranium from the same metals. The process is in all respects the same, and requires, therefore, no further description. It will be found much simpler and more convenient than that described by Rose, by means of carbonate of barium.

CHAPTER VII.

SILVER, MERCURY, COPPER.

SILVER.

Preparation of Pure Silver.

THE subject of the preparation of pure metallic silver has been studied in so exhaustive a manner by Professor Stas in his researches on the relations existing between atomic weights, that there is really absolutely nothing left for any other investigator to do in this subject. In the following pages are given an abstract of the processes which he found most successful. All the methods recommended for the preparation of pure silver which are capable of being executed on a large scale furnish an impure metal unless important modifications are introduced.

Preparation of Silver from Chloride of Silver.—All processes which depend upon the reduction of chloride of silver yield a metal containing copper and iron, unless, indeed, it has been re-dissolved three or four times succesively in nitric acid, the solution, after diluting with twenty or thirty times its weight of water, being each time poured into aqueous hydrochloric acid, and the chloride of silver violently agitated in the liquid, as in the process of assaying. Experience has shown that chloride of silver, free from copper and iron, can be obtained directly by pouring a cold solution of nitrate of silver diluted with thirty times its weight of water, into a slight excess of hydrochloric acid, washing the precipitate with cold distilled water, and then digesting the chloride, dried at the ordinary temperature, and finely powdered, in aqua regia. When well washed after this treatment, the chloride does not retain the slightest trace of either copper or iron; whilst, so long as the chloride of silver is in a curdy form, it retains in its pores, like coagulated albumen, some of the bodies which were dissolved in the liquid from which it was precipitated. Chloride of silver, however, when dried at the ordinary temperature and finely powdered, very easily yields to aqua regia foreign metals which contaminate it. But whatever may be the purity of chloride of silver, it produces a metal which always contains silicium and iron when it is reduced by Gay-Lussac's method; that is to say, by ignition with a mixture of chalk and charcoal.

The presence of these foreign matters is easily ascertained by dissolving 100 grammes of silver in pure nitric acid in a platinum dish, and

evaporating and fusing the nitrate. On dissolving the salt in cold water there is always a residue of silicic acid and sesquioxide of iron. M. Stas says that he has found as much as 15-100,000ths of silicium in silver reduced from the chloride by Gay-Lussac's process.

It is probable that the presence of so large a quantity of silicium in the metal so prepared is due to the action which silver has upon silicic acid. At the temperature necessary for fusion silver may reduce the silicic acid with formation of silicate and silicide of silver. Furthermore, the presence of carbon may favour the reduction of silicic acid and the formation of silicide of silver. One thing is certain, that the vapour of silver attacks silicic acid and the silicates. White porcelain becomes coloured yellow or yellowish-brown, and increases very sensibly in weight, when there is directed upon it the vapour of silver driven off before the oxyhydrogen blowpipe.

Chloride of silver, purified by the above process, mixed with its own weight of pure dry carbonate of sodium, containing a tenth part of pure nitrate of potassium, when heated in a white unglazed porcelain crucible, with the precautions recommended by Berzelius for avoiding intumescence, yields an ingot of silver. This ingot, fused again with a tenth of its weight of pure nitre and borax, and then run into an ingot-mould lined with pipe-clay, gives a bar of silver which retains scarcely any appreciable traces of foreign matters. This process requires great care, for when the mixture of chloride and carbonate is heated, if the temperature is raised too much at first, the mixture fuses, bubbles up, and is in danger of running over. To effect with safety the reduction of chloride of silver in a white unglazed porcelain crucible, the latter should be placed inside a clay crucible. The most convenient plan for performing this operation is the following:—Fill up the space between the two crucibles with calcined pipe-clay, powdered and mixed with 5 per cent of fused and powdered borax. Under the influence of the heat the borax fuses and solders the whole together. When the chloride of silver is reduced, the whole can be handled and the melted silver poured out as if it were one crucible. The great bulk which has to be heated before reaching the porcelain crucible prevents it cracking, and avoids loss of silver.

Preparation of Silver by Liebig's Process.—This process consists in reducing in the cold, by means of pure milk sugar, a pure concentrated ammoniacal solution of nitrate of silver, to which pure potash has been added, until fulminating silver begins to be precipitated. After a short time a violet precipitate is formed, which is transformed into a mirror of silver, if the solution does not contain more than 10 per cent of nitrate. If, on the contrary, it contains much more metal, the silver remains as a violet precipitate. This precipitate, after being washed with water, is digested with

aqueous ammonia, which removes the copper, if the silver contained any. When dried, it preserves its violet colour, and constitutes a peculiar modification of silver. Heated to 300° or 350° C., the metal becomes incandescent, and then assumes its proper colour, being of a dead white. To reduce it to bars fuse it with a certain quantity of pure nitre and borax, and run it into an ingot-mould lined with pipe-clay. This always gives the metal of a uniform purity. It must be borne in mind that it is not only necessary for the metal obtained by any process always to possess the same properties; it is also necessary for it to be absolutely identical with pure silver prepared by other methods. For it may happen—and this is the case in the reduction of pure chloride of silver by Gay-Lussac's process—that the operation of reduction communicates to the metal as much impurity as has been separated by solution and precipitation.

Preparation of Silver by Electrolysis.—Another plan consists in procuring the metal by the electrolysis of pure argentocyanide of potassium or of ammonium. This method is, however, long and very costly. The deposit is made upon a surface of porcelain previously covered with a mirror of silver, by Liebig's method. For a positive electrode coke is used, obtained by heating the vapour of naphtha to redness. To obtain a nitrate of silver fit to prepare the cyanide, dissolve in nitric acid silver assaying 999. Evaporate the solution to dryness and fuse the salt. After cooling, powder, and digest it in cold water, taking care not to dissolve it all, for otherwise oxide of copper would come into solution. The solution of silver is allowed to stand for three or four days, filtered through double filter-paper, then digested with an excess of oxide of silver, and allowed to remain at rest for a sufficient time. This solution is diluted with water until it only contains a thirtieth part of its weight of nitrate, and poured into pure aqueous hydrocyanic acid until cyanide is no longer precipitated. The cyanide is shaken in the liquid to finely divide it, and then washed with water acidulated with nitric acid, and finally with pure water. The cyanide is diffused in an amount of aqueous hydrocyanic acid equal to that used in its precipitation, and then pure ammonia or potash is added to the mixture until the cyanide is all dissolved. When undergoing electrolysis the positive pole of carbon is surrounded with cyanide of silver, contained in a linen bag purified by means of hydrochloric acid. Silver is thus returned to the liquid as fast as it is removed by electrolysation. M. Stas says that he has been unable to find any foreign body in this silver after it has been fused in an unglazed porcelain crucible with a mixture of purified nitre and borax.

Preparation of Silver by Precipitation with Phosphorus.—An excellent, although very slow, method for preparing perfectly pure silver is by acting on a 1 per cent solution of nitrate of silver with finely-divided phosphorus. This action is very slow, but the metal, after having remained for

a long time in an excess of solution of silver, and then being digested in ammoniacal water, yields, after fusion with purified nitre and borax, silver absolutely pure.

Preparation of Silver by Reduction of the Chloride in the Wet Way.—Dissolve at the boiling point silver coin in very dilute nitric acid. The nitrate of silver produced, after having been evaporated to dryness and fused, is kept at its point of fusion as long as any oxygen compounds of nitrogen are given off. The nitrate mixed with nitrite is dissolved, when cool, in the smallest possible quantity of cold water, and the solution, after resting 48 hours, is filtered through a double filter to separate all the matter that might have remained in suspension. The limpid solution, diluted with 30 times its volume of rain water, is precipitated by an excess of pure hydrochloric acid. The chloride of silver formed is, when deposited, washed by decantation, first with water acidulated with hydrochloric acid, and then with pure water.

This washing is performed by shaking the chloride violently each time in large stoppered bottles, with the necessary quantity of liquid.

It is then spread upon a cloth that has been washed with hydrochloric acid, strongly compressed and left to dry spontaneously. When perfectly dry it is finely powdered and digested for several days in aqua regia. It is then again washed in distilled water.

As the reduction by heat of chloride of silver with carbonate of sodium is a most delicate operation, when performed in large quantities, this reduction is effected under the influence of a solution of caustic potash and sugar of milk, as first proposed by Levol.

To procure potash and sugar of milk free from heavy metals, add to a concentrated solution of hydrate of potassium, previously boiled, a slight excess of a solution of sulphydrate of potassium to precipitate traces of dissolved metals.

After the deposit of the metallic sulphides, decant the alkaline solution and put it in contact with freshly precipitated oxide of silver, to deprive it of the sulphydrate of potassium; after a sufficient digestion and rest, separate the excess of oxide of silver and the sulphide of silver that has been produced. By the same means the heavy metals contained in an aqueous solution of sugar of milk are eliminated.

The chloride of silver contained in a large porcelain jar is digested at a temperature of from 70° to 80° C. with a mixture of solutions of hydrate of potassium and sugar of milk, until all the chlorine is separated from the silver. The metallic silver, which is grey, is washed with water until the excess of alkali has disappeared, then digested with pure dilute sulphuric acid, and lastly washed with ammoniacal water. After being dried, 5 per cent of its weight of borax is added, containing 10 per cent of nitrate of

sodium, and then, with necessary precautions, it is fusèd in a Paris crucible.

The fused metal may then be poured into a mould coated with a paste of mixed calcined and uncalcined kaolin. The bars of silver, first cleaned with sharp sand, are then heated to redness with caustic potash from tartar; the adhering kaolin having been dissolved, the bars are washed in pure water.

Preparation of Pure Silver by Reduction of its Ammoniacal Solutions.—This method furnishes pure silver more easily and promptly than any other known way; and it has the special advantage of giving it in a state of rare purity. It is based upon the complete reduction which ammoniacal solutions of silver compounds undergo when added to ammoniacal cuprous sulphite, or to a mixture of sulphite of ammonium and any ammoniacal salt of copper. At the ordinary temperature this reduction takes place slowly, with deposition of black, blue, or grey silver, according to the dilution of the liquids. Above a temperature of 60° C. the reduction is almost instantaneous, and the silver is precipitated in a state of division corresponding to the dilution of the liquid; its colour varying from grey to pure white.

Silver coin is dissolved in dilute and boiling nitric acid; the solution of nitrates of silver and copper is evaporated to dryness, and the saline mass fused. This fusion is necessary to destroy the nitrate of platinum, which is often formed in dissolving silver coin.* After cooling, the nitrates are taken up by an excess of ammoniacal water. The ammoniacal solution is left to rest for 48 hours. The limpid liquid is filtered through double filter paper, and then diluted with distilled water until it contains no more than 2 per cent of its weight of silver.

Neutral sulphite of ammonium is obtained by mixing ammonia with sulphurous acid. To ascertain the quantity of sulphite required for the complete precipitation of the silver from the ammoniacal solution of nitrate of silver and copper, heat to the boiling point a definite volume of solution of sulphite of ammonium, and ascertain the volume of the solution of silver and copper which is decolourised by this salt. Experiment has proved that, so soon as the sulphite of ammonium, sufficiently heated, is not coloured blue by the cupric oxide dissolved in the ammonia, there remains no trace of silver dissolved in the liquid, because in this case all the copper exists in the cuprous state, the presence of which is incompatible with that of any compound of silver dissolved in ammonia.

The quantity of sulphite of ammonium necessary for the precipitation of the liquid having been determined, add it to the argentiferous solution, and after being well mixed leave it to itself for 48 hours in a closed glass flask,

* Silver coin frequently contains iron, nickel, and traces of cobalt, platinum, and gold.

to prevent the contact of the air. At the end of this time about a third of the silver will be reduced, at the ordinary temperature, and is precipitated in the form of a shower of crystallised silver, of a greyish-white colour and very brilliant.

The decanted blue liquid, in quantities of ten litres at a time, is then put into a water-bath at a temperature of from 60° to 70° C. The time required to cause the elevation of temperature is quite sufficient for the complete reduction of the remainder of the silver in solution, and for the reduction of the cupric sulphite to the state of cuprous sulphite, especially if care is taken to have a sufficient excess of solution of sulphite of ammonium. The liquid in which the reaction takes place becomes quite colourless if the copper contains neither nickel nor cobalt. If it contains nickel, it takes a slight green tint; it takes, on the other hand, a reddish tinge if cobalt is present.

The silver being separated out, decant the liquid when cold, and wash separately the silver precipitated from the cold and the warm solutions. This washing is performed by decantation with ammoniacal water; it is continued as long as the washing waters are perceptibly coloured blue by exposure to air, or are precipitated by chloride of barium. The silver is afterwards left for several days in concentrated ammonia, and then washed in pure water.

If the solution from which the silver is precipitated has been diluted until it contains no more than 2 per cent of silver, the ammonia left in contact with this metal is not coloured even after several days' digestion. There is no longer any copper for the ammonia to dissolve; it dissolves silver instead, for this metal is feebly attacked by the alkali under the influence of air, as is easily proved by evaporating liquid ammonia which has remained several days in contact with turnings of pure silver. The liquid always leaves a black shining mirror of nitride of silver by its spontaneous evaporation.

By fulfilling all the conditions above described, and especially by carrying the dilution of the ammoniacal solution of the nitrates of silver and copper to 2 per cent of silver, we obtain silver of a rare purity. When the precipitated silver is required in bars, fuse it with 5 per cent of its weight of calcined borax containing 10 per cent of nitrate of sodium, as mentioned in the case of the silver reduced from the chloride by potash and sugar of milk. Larger quantities may also be fused with the aerhydrogen blowpipe in a crucible of pure porcelain, or in an oxyhydrogen gas furnace in crucibles of marble-lime.

Purification of Silver by Distillation.

Pure silver may be fused in air at a temperature sufficiently high to volatilise it, without becoming at all stained or discoloured, and without

giving off coloured vapour. This fact has been taken as a basis by Professor Stas, in order to ascertain the purity of the silver prepared by either of the processes already given. He describes his experiment as follows:—About 400 grammes of silver reduced from its chloride, placed in a crucible of lime from white marble, itself enclosed in a refractory crucible, were submitted to the hissing flame produced by the combustion of ordinary coal gas with pure oxygen. The silver fused without becoming in the least discoloured. It was then heated until it boiled violently. The silver first gave to the flame the sodium character; but in a short time the yellow colour disappeared, and, so long as the silver did not boil, no discolouration appeared, although the metal gave off vapour in considerable quantity. After the silver boiled, a pale blue vapour was produced, which occasionally bordered upon purple. Some chemists assign a green colour to the vapour of silver. The green colour observed arose indisputably from the copper contained in the silver submitted to the experiment. The purple colour is attributed to the existence of strontium or lithium in the marble used for the preparation of the quick-lime crucible.

This vapour stained the lime a deep yellow, which colour, however, disappeared on the application of heat. When, by this process of refining, the silver had lost all volatile matter, and when the fixed but oxidisable materials that it might contain must have united with the lime, it was poured from a good height, and in a thin stream, into distilled water, where it took the form of pure white, almost spherical globules. The crucible presented no trace whatever of a metallic oxide or silicate.

The same treatment was applied to the pulverulent silver prepared by the cuprous ammoniacal sulphite, and identical phenomena presented themselves, excepting always the intense yellow colour of the flame, which was produced when the silver reduced from the chloride was heated to near its boiling point.

Before submitting the silver under experiment to the action of the oxyhydrogen gas-flame care must first be taken to expose the lime crucible to the heat of the oxyhydrogen blowpipe, so as to eliminate as much as possible from the lime the volatile substances that give a particular colour to the flame; all marbles contain notably sodium, and many contain strontium and lithium.

Having been struck by the facility with which silver may be boiled violently, and distilled in the flame of oxyhydrogen gas, Professor Stas was led to experiment on the distillation of silver both for the object of obtaining it absolutely pure, and also to ascertain if silver refined by the methods already described still retains any traces of fixed bodies capable of uniting with lime.

For this purpose, in a block of lime prepared from white marble, of from

25 to 30 centimetres in length, by 10 centimetres width and height, there was made a circular cavity 3 centimetres in diameter and 2 centimetres in depth, in communication with an inclined plane also 3 centimetres in width, by at most half a centimetre in depth, and serving to condense the vapour of silver. This inclined plane was terminated by a reservoir acting as a receiver for the liquid metal. About 50 grammes of refined silver were placed in the cavity, first heated to whiteness by the application of a jet of coal-gas burning in a suitable excess of compressed air, and the block was covered with a plate of lime from white marble, 5 centimetres in thickness, pierced with two inclined circular openings, one corresponding to the circular cavity, the other to the little reservoir at the end of the inclined plane. Through one of the openings of the plate was passed a large oxyhydrogen blowpipe, furnished with very thick ends of platinum to avoid their fusion and the transportation of the metal. When the interior of the cavity had been heated to the boiling point of silver, not more than ten or fifteen minutes were required to distil the whole of the silver. The 50 grammes were volatilised without leaving in the cavity of lime, which was used as the retort for distillation, the slightest appreciable residue to the eye assisted by a glass. The distillation of silver is such a simple operation to manage that nothing could be easier than to procure a kilogramme of distilled silver, if the apparatus was proportioned to the mass. In the operations above described, *at least* half the silver used was, however, lost. It was, in fact, carried away in the state of pale blue vapour by the current of oxyhydrogen gas, although this was very moderate, and without too great an excess of oxygen; it was diffused through the surrounding atmosphere, the transparency of which it affected, while imparting to it a very sensible metallic taste. The apparatus was also very imperfect; vapour of silver escaped in quantities by the opening intended to carry off the products of combustion, and all round between the block and the thick plate serving as a cover to it. Their surfaces, indeed, were not sufficiently well smoothed to fit very exactly. Wherever the vapour of silver passed it left a light or dark yellow stain, like that left by the vapour of litharge. The condensation of the vapour of silver takes place the more readily the less excess of oxygen the oxyhydrogen gas contains.

All the different samples of silver prepared by any of the above described methods were subsequently fused, and cast in an ingot-mould lined with white pipe-clay. To detach the pipe-clay, the surface of the bars were rubbed with sharp white sand. They were then heated to dull-redness and covered over with caustic potassa, which was kept in a fused state for at least a quarter of an hour. The adherent pipe-clay being in this manner attacked, the bars were suddenly plunged into water. The silicate formed

on the surface being thus detached, the bars, after a second scrubbing with sharp sand, were fit for use. These bars, before being employed, were treated with boiling hydrochloric acid, washed first in cold aqueous ammonia, then in pure water, and finally heated to redness on plates of pure silver. It having been necessary for the silver to be in the form of small lumps, from 2 to 25 grammes in weight, in the form of sheet, and in a certain state of division to make up weights previously calculated; the small lumps were obtained by cutting the ingots with a chisel on an anvil of polished cast-steel. The turnings and filings obtained from the ingots by means of a lathe and file furnished the finely-divided silver. To separate the iron adhering to the silver when cut with the chisel, lathe, or file, these different forms of the metal were digested in a close vessel for twenty-four hours, and at a temperature of 60° to 80° C., first with strong hydrochloric acid, and then with pure ammonia. The silver was finally washed with absolutely pure water, heated to redness on a plate of pure silver, and immediately put into bottles with well-fitting stoppers. Having found that silver, after having been rolled, contained iron, which was absent before rolling, the precaution was taken to have all the silver which was required in the form of sheet rolled between two plates of pure silver. It is only at the expense of the surfaces of the two plates which touch the cylinders of the mill that the surface of the inner plate could be protected from contamination with all foreign metal. The laminated silver was heated to redness in the air, and enclosed whilst very warm in a well-stoppered bottle.

Ascertaining the Purity of Silver.—Professor Stas gives a very simple plan for ascertaining the purity of silver. The pure metal remains melted in the air at a sufficiently high temperature to volatilise it without being covered by any scum or colouration, and without giving a coloured vapour. Silver containing no more than the 500,000th part of iron, copper, or silicium becomes covered with a very strong and mobile scum when it is fused before a blowpipe, fed with a mixture of illuminating gas or hydrogen and an excess of air. Silver containing scarcely appreciable traces of copper when volatilising in an oxidising flame always gives a coloured flame. This assay may be performed on charcoal or white-burned pipe-clay, or on porcelain, by means of a gas blowpipe or a simple eolipyle. The scoria derived from the impurities in the metal always forms upon the surface of a flattened spheroid caused by the fusion. After cooling, the foreign matter is found adhering to the silver near the point of contact of the metal with the support.

Estimation of Silver in the Metallic State.

According to Dr. A. Classen, silver is wholly precipitated by cadmium. When dealing with a nitric solution of silver, evaporate to dryness in the

presence of sulphuric acid, dissolve the sulphate of silver in boiling water, plunge into it a plate of cadmium, and the reduction of the silver takes place at once. The silver is deposited in a compact mass, easily washed with water; as it may contain a little cadmium, boil it in the acid liquid until no hydrogen escapes; wash it until the water contains no sulphuric acid; then dry and calcine; the silver, at first a black grey, takes the metallic lustre; it may then be weighed—the results are very exact.

The reduction of silver compounds by means of cadmium goes on very quickly, and as cadmium is but slightly soluble in dilute acids, the same piece of metal will serve for several operations, without even losing the metallic lustre of the surface. Freshly precipitated chloride of silver may be reduced in the same way.

Volumetric Estimation of Silver.

It would be out of place here to describe the well-known Gay-Lussac process for the assay of silver by the wet way. It is necessary, however, to draw attention to some recent improvements introduced into this process by Professor Stas, by which the errors incidental to the old process are entirely obviated. The operation is conducted in the following manner:—The silver, after having been heated to redness in a crucible of the same metal and properly cooled in the air, is weighed and introduced into a white glass flask, with the stopper well ground in with emery, and having very thick sides to enable it to withstand an internal pressure of at least ten atmospheres. Then pour upon the metal ten times its weight of pure nitric acid at 25° Baumé. Put in the stopper and fix it solidly in its place by the aid of strong cord. Then surround the flask with wire gauze, and place it in a bath where its temperature is raised to 45° or 50° C. At the end of twenty-four or thirty-six hours all the silver will have dissolved without any trace of gas developing itself, and consequently without anything escaping from the flask. Indeed, the binoxide of nitrogen, as fast as it is produced, reduces the nitric acid to the state of nitrous or hyponitric acid, which at this temperature remains perfectly dissolved in the large excess of nitric acid employed. If the temperature of the bath does not exceed 50°, there is nothing to fear. Upwards of a hundred solutions of silver in a closed flask have been made, employing from three to fifty grammes of silver at a time, without any accident taking place. Twice only, the temperature of the bath rising much too high, two flasks which were immersed in it yielded to the internal pressure and produced a rather violent explosion. The plan of dissolving the silver in a close vessel has been adopted because the method of solution in open vessels, such as is adopted in the assay rooms of the Mint, causes a slight loss of silver. Moreover, the constant presence of silver in the washing-waters of the gas,

arising from the solution of the metal in the ordinary way, sufficiently point out the necessity of effecting this solution either in a close vessel or in apparatus in which the escaping gases may be washed. It ought to be added, however, that the loss experienced upon a gramme of silver never affects the accuracy of the assay of silver in the Mint, owing to the much more considerable and unavoidable errors of experiment.

The remainder of the description is given in Professor Stas's own words :—

"The solution of the metal having been effected, and the flask well cooled, I introduce such an amount of pure water that, with the acid already added, the total weight of the liquid becomes at the minimum thirty-five times, and at the maximum fifty times, the weight of the silver employed. I now carry the flask into a dark room lighted with gas. After having conveniently inclined it, I introduce into it a tube, sealed up at one end, fixed to a rod of platinum, and containing the chloride weighed with the greatest accuracy which my balances will admit of. I then drop the chloride into the solution of silver, and wash the tube out several times with water, so as not to lose the traces of chloride which may remain adhering to it. After having tightly closed the flask, and enveloped it in caoutchouc, I shake it until the liquid, at first turbid, becomes perfectly clear. I then proceed to the assay of the silver remaining unprecipitated. For this purpose I have prepared with the greatest care the decimal solutions of salt and silver, such as are employed in the laboratories of the Mint.

"On the other hand, I have myself manufactured pipettes, tubes which when empty in a vertical position, would furnish me ten, five, four, three, two, one, or half a cubic centimetre of decimal solution. I also constructed burettes, which, when placed in a vertical position, would deliver drops exactly equal to the twentieth of a cubic centimetre. The burette itself and the tubes of half, one, and two centimetres, are subdivided into twentieths of a cubic centimetre. The small burette consists of a graduated tube of four or five millimetres internal diameter, drawn out to a point so as to expose an opening of about one millimetre in diameter, and melted to a larger open tube, the aperture of which is covered with a piece of vulcanised caoutchouc folded over the side of the tube, and more or less strongly bound to it, according as it is wished to deliver the drops more or less rapidly; my burettes would only give five or six per minute.

"It is absolutely necessary to hold the burettes in a vertical position, for the same instrument which furnishes with the greatest accuracy twenty drops per cubic centimetre only delivers seventeen or eighteen when it is inclined 45°; in a position of 10° or 15° no more than sixteen or seventeen drops are required to make a centimetre.

"To perform the assay, I had besides the following arrangement :—In a long narrow box, the anterior portion of which was furnished with yellow

glass, and the posterior portion lighted by a gas lamp, I arrange a perfectly spherical glass globe containing a saturated solution of the double chromate of potassium and sodium, so as to concentrate the rays and obtain a cone of yellow light. I then place the flask containing the assay in such a position that the surface of the liquid may be traversed by the beam of yellow light. To make an observation, I place myself so as to make an angle of 60° with the luminous ray traversing the flask. When this artifice is employed, a liquid containing two miligrammes of silver per litre produces a yellow opaque and dull precipitate of chloride of silver, when half a centimetre of decimal solution is allowed to fall carefully upon its surface; when the quantity of silver is reduced to one milligramme, the precipitate of chloride is yellow, opaque, and brilliant; when the liquid is diminished in strength, so that it contains no more than the twentieth of a milligramme of silver per litre, there is still produced an appreciable cloud upon the addition of a corresponding quantity of decimal solution. It is only necessary to wait sufficiently long, without touching the flask, to be certain of it. Nevertheless, in these assays I have only worked to tenths of a milligramme.

"In all my experiments I have continued adding decimal salt solution as long as I have seen a cloud produced on the surface of the liquid after standing fifteen minutes. When I have arrived at the extreme limit, and have just passed it, I add five centimetres of decimal solution of silver. After well shaking, I neutralise three-quarters of the excess of silver, so as to obtain immediately upon agitation a clear liquid approaching very nearly the extreme limit. When there was a difference between the results of two assays, a difference that has never exceeded two or three tenths of a milligramme, I always took the minimum result.

"Those who have made many assays by the wet way will have noticed that the interior sides of a flask in which they have for some time shaken chloride of silver produced by successive precipitation, becomes covered with a kind of varnish of chloride, appears greasy, and so loses its transparency. To obviate this inconvenience when it occurs, I remove, by means of a pipette, a portion of the liquid after it has been agitated and become limpid by standing sufficiently, and transfer it to a bottle having parallel glass sides, and ascertain in this second bottle the presence of silver or salt in excess. The liquid in this bottle was always added to the first whenever it was found necessary to continue the operation.

"The assay presents another difficulty which may lead one greatly in error when not forewarned of it.

"A liquid from which almost all the silver has been precipitated by a saline solution, but which still contains between 1 and 2 milligrammes of silver per litre, is precipitated equally upon the addition of a decimal

solution of silver or of salt. In this case, however, there is a very evident difference in the resulting turbidity. The precipitate occasioned by the decimal salt solution in the assay containing one or two milligrammes of silver in the state of nitrate is always opaque, yellow, and brilliant; whilst the precipitate formed upon the addition of nitrate of silver to the same liquid is whitish and translucid. I account for this anomaly by the slight solubility of chloride of silver in the alkaline nitrate in solution, and which precipitates in the presence of a silver solution richer than itself. I have, notwithstanding, always added decimal salt solution until precipitation ceases.

"Such is the method of assay which I have adopted for all my determinations by means of double decomposition."

In a note published subsequently to the above researches, Professor Stas shows how one of the difficulties in the wet assay of silver can be avoided. He says that the Gay-Lussac process is open, under certain conditions, to a source of error arising from the solubility of chloride of silver in the very liquid to which its origin is due. This solution, whatever its mode of production may be, is precipitated equally by a decimal solution of silver and by hydrochloric acid or an alkaline chloride. The extent to which this precipitation ensues is uncertain. At the ordinary temperature there may be a variation of from one to six-thousandths in 100 c.c. of the liquid. Practically, it is quite possible whilst preserving the simplicity of the wet method of assay to substitute a bromide or hydrobromic acid for a chloride or hydrochloric acid. This absolutely removes those anomalies which have been observed to be attendant on the use of a chloride or hydrochloric acid.

Extraction of Silver from Burnt Pyrites.

In the manufacture of sulphuric acid, iron and copper pyrites are burnt in kilns supplied with a limited amount of air, the products of combustion being thence conducted into leaden chambers, as in the case of vitriol manufactured from ordinary brimstone.

The resulting residue, or "burnt ore," was formerly to a large extent smelted for copper, and from the great amounts of oxide of iron present, acted as a valuable flux for the more siliceous ores of that metal. It may be taken as containing on the average about 4 per cent of copper and 18 dwts. of silver to the ton.

For several years past a large proportion of the burnt ore produced in the various chemical works of this country has been worked by what is known as "the wet process of extraction."

By this process the burnt ore is first finely ground and sifted, and subsequently roasted with common salt until, by the oxidation of the metallic sulphides present, a portion of alkaline salt is converted into sulphate

of sodium, whilst the copper is, on the contrary, transformed into a soluble chloride. The copper salt is subsequently removed by repeated washings, and the copper precipitated by iron in the metallic state. It has been long known to those engaged in this business that the copper precipitate produced not only contains a notable quantity of silver but also distinct traces of gold. No attempt, however, to separate the precious metals, and to turn them to profitable account, had been made until Mr. F. Claudet patented a process for the separation of silver from ordinary copper liquors by the addition of a soluble iodide.

The amount of silver present in burnt ore seldom exceeds 18 dwts. per ton; but, as the whole of this is never obtained in solution, it follows that, dealing with such minute quantities, in order to obtain satisfactory commercial results, the process employed should be both cheap and expeditious.

The vats, in which the burnt ore which has been roasted with salt is lixiviated, generally receive some eight or nine successive washings with either water or with water acidulated by hydrochloric acid, and of these the first three only contain a sufficient amount of silver to be worth working. For the purpose of removing the soluble salts from the ground and washed ore, hot water is employed, and as a large proportion of the chloride of sodium used remains undecomposed, it acts as a solvent for the chloride of silver produced during the process of furnacing.

The several operations for the extraction of silver are conducted in the following manner; and as the first three washings contain nearly 95 per cent of the total amount of that metal dissolved, these alone are treated.

The liquors are first run into suitable wooden cisterns, each of a capacity of about 2700 gallons, where they are allowed to settle. The yield of silver per gallon is now ascertained by taking a measured quantity, to which are added hydrochloric acid, iodide of potassium, and a solution of acetate of lead. The precipitate thus obtained is thrown upon a filter, and, after being dried, is fused with a flux, consisting of a mixture of carbonate of sodium, borax, and lamp-black. The resulting argentiferous lead is passed to the cupel, and, from the weight of the button of silver obtained, the amount of that metal in a gallon of the liquor is estimated.

The liquor from the settling-vat is now allowed to flow into another of slightly larger capacity, whilst, at the same time, the exact amount of a soluble iodide necessary to precipitate the silver present is run into it from a graduated tank, together with a quantity of water equal to about one-tenth the volume of the copper liquor. During the filling of the second tank its contents are constantly stirred, and, when filled, a little lime-water is added, and it is allowed to settle during 48 hours. The supernatant liquors are, after being assayed, run off, and the tank again filled, when the

precipitate collected at the bottom is, about once a fortnight, washed into a vessel prepared for its reception.

This precipitate is chiefly composed of sulphate of lead, iodide of silver, and salts of copper, from which the latter are readily removed by washing with water acidulated by hydrochloric acid. Thus freed from salts of copper, the precipitate is decomposed by metallic zinc, which completely reduces the iodide of silver, and, to a certain extent, also the sulphate of lead. The result of this decomposition is—

1st. Iodide of zinc, which, after being standardised, is employed in subsequent operations to precipitate further quantities of silver. 2nd. A precipitate rich in silver, and also containing a valuable amount of gold.

The results of nearly six months' experience of this process at the Widnes Metal Works show that ½ ounce of silver and 1½ grains of gold may be extracted from each ton of ore worked at a total cost, including labour, loss of iodide, &c., of 8d. per ton, or 1s. 4d. per oz. of silver produced. If from this amount be deducted 6d., the value of the 3 grs. of gold contained in each ounce of silver, the cost of production, per oz. of silver, will be reduced to 10d., and the expense of working a ton of ore to 5d. This leaves a profit of about 2s. on each ton of ore worked.

The value of the precious metals extracted from each ton of ore treated is certainly not large, as the amount originally contained is very small. With richer ores, however, more satisfactory results would be obtained; but when it is stated that some of the copper extraction works operate on 30,000 tons of ore annually, it becomes evident that a profit of 2s. per ton is a most important consideration in a business in which competition has rendered care and economy absolutely necessary.

Assay of Silver Ores.

See Separation of Lead from Silver.

MERCURY.

Estimation of Mercury in the Metallic State.

In estimating mercury by distillation it is necessary, especially if the metal is in the state of chloride or sulphide, to take certain precautions, without which a portion of the sulphide or chloride would volatilise without decomposition. H. Rose gives the following directions for carrying out the operation:—Introduce into a glass tube capable of resisting fusion, closed at one end, and measuring from 35 to 50 centimetres in length, a column of bicarbonate of sodium, then one of quick-lime, and then a well blended mixture of the mercurial compound and quick-lime, and, finally, a column of quick-lime. The open end of the tube is drawn out and bent round so as to enter a small flask containing water. The tube is heated as if for an organic analysis, commencing at the open end and finishing with the

bicarbonate of sodium. The operation ended, cut the bent end of the tube. Collect all the mercury in the flask, dry with paper, and afterwards over sulphuric acid, and then weigh it.

There is no need to replace the quick-lime by hydrate of lime. That would occasion all the inconvenience of an analysis of a sulphuretted combination of mercury. The water, acting on the sulphide of calcium, would form sulphuretted hydrogen, which, by dissolving in the water of the receiver, would, in time, transform a portion of the reduced mercury into sulphide. It is even advisable in this case to replace the bicarbonate of sodium by carbonate of magnesium.

Combinations containing iodide of mercury are not entirely decomposed when treated as above. Biniodide and protoiodide are condensed in the extremity of the tube simultaneously with the metallic mercury.

To analyse these combinations recourse must be had to metallic copper, the operation being similar to that with quick-lime.

Estimation of Mercury in the form of Protochloride.

M. de Bonsdorff has proposed to precipitate mercury as protochloride by alkaline formiates. This method may lead to completely erroneous results, as alkaline formiates do not invariably reduce bichloride of mercury. The affinity of mercuric chloride for alkaline chlorides is so great that when these bodies are present the ordinary reactions of mercury are not produced. When a liquid contains much hydrochloric acid, an alkali does not precipitate oxide of mercury from it. Sulphuric and nitric acids have the same effect. Such a mercuric solution, containing a large excess of potash, is not precipitated by sulphide of ammonium unless the base has been previously supersaturated with an acid.

The best method for estimating mercury is to precipitate it in the state of protochloride by phosphorous acid. When the liquid contains free hydrochloric acid, the temperature may be raised to 60° C., without the protochloride of mercury being reduced to the metallic state by phosphorous acid. The precipitated protochloride is not immediately formed in very weak liquids; it is necessary to leave the mixture undisturbed for twelve hours. The chloride deposits itself readily, especially when the liquid is sufficiently acid. The precipitate is to be collected on a filter, washed with cold, or even hot water, and dried at 100°. This process is very applicable to cases where the liquid contains much nitric acid. Only the solution must then be diluted with a sufficient quantity of water.

Separation of Mercury (Persalts) from Silver.

Add a sufficient quantity of hydrochloric acid to the diluted solution. After the deposition of chloride of silver, decant the supernatant liquid;

then heat the chloride precipitate with a small quantity of nitric acid, add some water and a few drops of hydrochloric acid, and then filter. Precipitate the mercury from the filtered liquid by phosphorous acid, according to Rose's process, already described.

Separation of Mercury from Zinc.

This separation may be readily effected by precipitating the mercury in the state of protochloride by phosphorous acid, in the presence of free hydrochloric acid. The process may be carried out as previously described.

COPPER.

Precipitation of Metallic Copper in Quantitative Analyses.

The estimation of copper in the state of oxide, simple as the operation appears, is, nevertheless, always more or less faulty, and the results are not sufficiently exact. After the oxide of copper has been precipitated by potash and calcined, the filter in which the oxide is retained, and from which it is impossible to detach it, reduces a portion of the copper. The metal must therefore be re-oxidised. But calcining in a vessel open to the air, or even in a current of pure oxygen, will not completely re-form the oxide. The oxygenation of the metal remains imperfect, however long the reaction may be continued. Recourse must now be had to nitric acid, whose oxidising action is perfect; but another inconvenience then arises. When the nitrate of copper is decomposed some of the oxide is carried off in the stream of nitrous vapours. This phenomenon is shown very visibly by experimenting in a small glass flask holding 100 c.c., with a neck 7 or 8 centimetres long. However carefully the decomposition of the nitrate may be conducted, the interior of the flask and its neck are entirely covered with an impalpable powder of cupric oxide, some even escaping from the flask in appreciable quantities.

On very carefully experimenting in a comparatively large and well closed platinum crucible there is a notable loss. Thus, according to some experiments of MM. Millon and Commaille, 1·3305 grms. of pure copper gave but 1·6605 grms. of oxide instead of 1·6675 grms.

To obviate these difficulties copper should be estimated in the metallic state. The oxide is precipitated by potash, and the precipitate, washed with hot water and dried, is burnt, with the filter, in a large platinum capsule. The residue of this calcination does not adhere to the sides of the capsule. It is placed in a platinum vessel, where it is reduced by a current of pure hydrogen.

Precipitation of Copper as Sulphide.

This would be an excellent form in which to estimate copper were it not that, on the ignition previous to weighing it, the sulphide oxidises and loses

sulphur, the result being a mixture of disulphide, sulphate, and oxide. David Forbes has shown that this difficulty can be got over in a similar manner as in the case of nickel (see p. 148). The weight of sulphur in the sulphide of copper and of oxygen in the oxide being identical, a mixture of sulphide and oxide in varying proportions may be weighed and calculated as if it were pure oxide or pure sulphide. It is only necessary, therefore, to remove the small quantity of sulphuric acid in the ignited sulphide of copper. This is effected by adding a small amount of carbonate of ammonium to the incinerated sulphide as soon as it is cold, and then carefully heating until all ammoniacal salts are expelled. Some attention must be paid to the details of the operation, as the sulphide of copper, especially in cases where free sulphur has been precipitated along with it, is very apt to aggregate together or even fuse during the incineration (if this is not very carefully conducted), and, consequently, it is less easily acted on by the air during incineration; this must be avoided, and the oxide should also not be allowed to absorb hygrometric moisture before or during weighing.

Instead of precipitating copper from solution, in presence of other metals, with zinc, its separation is more conveniently effected by means of an electric current. The slightly acid solution of the sulphates of copper and other metals is contained in a platinum crucible which forms the negative pole of an electric current from two of Bunsen's cells; the positive pole terminates in platinum foil, and passes through a perforation in a watch-glass which covers the crucible, dipping into the liquid. The copper separates in a perfectly pure state, and the reduction is accomplished in 3 or 4 hours. The intensity of current, concentration of solution, temperature, and amount of free acid may vary within wide limits without impairing the accuracy of the result.

Volumetric Estimation of Copper.

Mohr's method of estimating copper, by adding a standard solution of cyanide of potassium to an ammoniacal solution of copper, Herr Fleck says, offers two objections; the quantity of cyanide necessary to destroy the blue colour varies according to the quantity of ammonia the liquid contains, and at the end of the operation it is difficult to tell the exact moment at which the blue colour disappears. To remedy these inconveniences, Herr Fleck proposes to dissolve the copper compound in carbonate of ammonium instead of ammonia. He shows that an excess of this salt does not interfere with the reaction. In the second place, he adds a drop of ferrocyanide of potassium to the blue liquor, and then at the moment the cupro-ammoniacal compound is destroyed the liquid becomes red.

Estimation of Copper with Bichloride of Tin.—F. Weil has proposed a new method for the volumetrical estimation of copper, which is based on

the two following facts :—(1) In the presence of free hydrochloric acid, and at a boiling heat, the slightest trace of chloride of copper which may be present causes the liquid to assume a marked yellow-greenish tinge, and this is the stronger the more hydrochloric acid is present. (2) Protochloride of tin causes, at that temperature, the immediate reduction of the salts of oxide of copper dissolved in hydrochloric acid to salts of the suboxide of copper, which, in solution, are absolutely colourless. Any single drop of chloride of tin added in excess may be at once detected by the addition of a drop of a solution of bichloride of mercury, which causes the precipitation of calomel. If the solution of copper contains a persalt of iron also, the quantity of chloride of tin employed will indicate the joint quantities of iron and copper present.

Estimation of Copper with Ferrocyanide of Potassium.—When the ore of copper, after having been acted upon by acids, is treated with excess of ammonia in order to precipitate the oxide of iron, that substance invariably retains larger or smaller quantities of the oxide of copper. The quantity thereof so retained varies according to the larger or smaller quantity of copper contained in the ores. It is hence necessary to repeat the treatment with ammonia at least twice, sometimes even three and four times, in order to obtain a complete separation of copper from iron.

In order to obviate the loss of time which is caused by these operations, M. Maurizio Galetti, Chief Assayer and Chemist to the Royal Assay Office at Genoa, proposes to convert into acetate the small quantities of oxide of copper which accompanies the precipitate of oxide of iron. This can be effected by two different methods, dependent on the fact whether the oxide of iron is removed by filtration (previous to the use of standard solution of ferrocyanide of potassium), or is left in the ammoniacal liquid. The operations are conducted as follows :—

1. Suppose a copper pyrites be submitted to analysis. Take 1 grm. of the previously very carefully pulverised and dried ore. Treat it first with concentrated nitric acid, boiling to incipient dryness, in order thereby to free the sulphur from any small particles of ore which are at first taken up by it. Add 10 c.c. of hydrochloric acid, boil down to about half that bulk, dilute with distilled water, and next add ammonia in large excess ; boil the fluid, and next add acetic acid until the liquid assumes an emerald-green colour. After the liquid has been well stirred, boil again for about 2 minutes ; and again add ammonia in excess. The liquid is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the fluid up to ½ litre. This having been done, the fluid is very cautiously and gradually acidified with dilute acetic acid. Any considerable excess of this acid should be avoided. As soon as the basic acetate of iron has subsided, the precipitation of the

copper by means of the standard solution of ferrocyanide of potassium is proceeded with.

Since the oxide of copper which might have adhered to the oxide of iron has been converted by the process just described into a soluble salt, it cannot fail to be completely precipitated by the ferrocyanide of potassium solution. When a determination of copper has to be made in ores which are rather poor (that is to say, contain less than 6 per cent of copper), it is preferable to add to the nitric acid solution 0·1 grm. of pure copper, which quantity has to be deducted afterwards from the results obtained. This precaution is required in order to prevent the presence of a large quantity of oxide of iron from vitiating the results of analysis of poor ores. When ores contain up to 12 per cent of copper, a quantity of 1 grm. of the ore should be taken; but, for richer ores, 0·5 grm. is sufficient. It is always advisable to make a control analysis with pure copper at the same time while testing the ores.

2. The second modification is carried out in the following manner:—

After the second addition of ammonia to the liquid, it is filtered, and the precipitate is washed with a dilute and boiling solution of acid acetate of ammonium. This solution is prepared by saturating 20 grms. of pure acetic acid with ammonia, and adding thereto 15 grms. of pure acetic acid in 585 grms. of water. When the washing of the oxide of iron is carefully done, the salt of copper, which tenaciously adheres to the oxide of iron, is entirely removed therefrom; but it will require about 400 grms. of the fluid, the preparation of which has just been described.

The normal solution of copper for standardising the ferrocyanide of potassium should be prepared as follows:—

0·2 grm. of pure copper is dissolved in nitric acid; excess of ammonia is added; the fluid next acidified with acetic acid, then diluted with 400 grms. of acid acetate of ammonium, and the whole brought up to 500 grms. To this solution 20 c.c. of the standard solution of ferrocyanide of potassium are added, when the liquid should not contain any excess of either copper or of ferrocyanide.

The standard solution of ferrocyanide of potassium to be used for the determination of copper is made by dissolving 50·225 grms. of ferrocyanide in as much distilled water as will suffice to make the solution weigh exactly 1 kilogramme.

If the copper ores contain zinc, nickel, and cobalt, the copper should be first separated from these metals, either by precipitating the copper from its solution by means of zinc, or as sulphide of copper by means of hyposulphite of sodium.

Estimation of Copper with Sulphide of Sodium.—An ammoniacal solution containing 1-10,000th of copper reacts distinctly on moist, recently-

precipitated sulphide of zinc—the zinc dissolving, while the copper is precipitated in the form of sulphide. Sulphide of zinc decomposes instantly in a hot ammoniacal solution of copper.

Starting from this reaction, Dr. C. Kunsel proposes the following volumetrical method for the estimation of copper:—

He prepares pure sulphide of sodium by saturating a solution of caustic soda free from carbonate, with sulphuretted hydrogen, and driving off the excess of the gas. The solution is then diluted so that a cubic centimetre precipitates a centigramme of copper.

A known weight of pure copper is dissolved in nitric acid, the solution supersaturated with ammonia, diluted, and heated to boiling. The solution of sulphide of sodium is then added to the hot solution of copper, stirring continually until a drop of the mixed solutions no longer colours sulphide of zinc brown. Sulphide of zinc for indicating the complete precipitation of the copper is prepared in the following way:—Zinc is dissolved in hydrochloric acid, the solution is supersaturated with ammonia and is then boiled with a little sulphide of zinc to remove the lead which is always present in commercial zinc. The ammoniacal solution of zinc, now free from lead, is filtered, and decomposed with sulphide of sodium, a small quantity of zinc being allowed to remain in solution. The moist sulphide of zinc, with excess of zinc solution, is then spread evenly upon filter paper several layers thick. When the paper has absorbed most of the solution the moist white layer of sulphide of zinc is ready for use.

The ore or alloy, freed from arsenic, is dissolved in hydrochloric acid with the addition of some nitric acid, and, when necessary, is evaporated to dryness, the deposit dissolved in hot water, and filtered to separate silica. Any iron may be removed from the mixed chlorides by the addition of ammonia. The solution freed from iron is then rendered strongly ammoniacal, heated to boiling, and the standard solution of sulphide of sodium added (with continual shaking) until a drop of the mixed solutions no longer acts on sulphide of zinc, *i.e.*, until all the copper is precipitated. The number of cubic centimetres of the standard solution is then read off and the amount of copper calculated.

Assay of Copper Pyrites.

The following method of treating copper pyrites has been found more advantageous than the ordinary process of oxidising the mineral with aqua regia, and subsequently evaporating the solution repeatedly with chlorhydric acid, or with sulphuric acid, to expel the last traces of nitric acid. It is thus described by Mr. F. P. Pearson in the "Chemical News":—

Place a weighed quantity of the powdered mineral, together with some chlorate of potassium, in a porcelain dish. (Five grammes of a variety of

a pyrites containing about 18 per cent of copper was found to be enough for one analysis; and a quantity of chlorate of potassium equal to a small tea-spoonful was added to the ore.) Invert a small glass funnel with bent stem in the dish above the pyrites, and pour upon the latter rather more ordinary strong nitric acid than would be sufficient to completely cover the powder. Place the dish upon a water-bath, and, from time to time, throw into it small quantities of chlorate of potassium. The doses of the chlorate must be repeated at frequent intervals, until free sulphur can no longer be seen in the dish. If need be, add nitric acid, also, from time to time, to replace that lost by evaporation.

As a general rule, it is safer and more convenient to heat the mixture on a water-bath than upon sand, though the oxidation of sulphur can be effected more easily and quickly when the mixture of nitric acid and chlorate is heated to actual boiling than at the temperature obtainable hy means of a water-bath. When the last particles of sulphur have been destroyed, remove the inverted funnel from the dish, rinse it with water, and collect the rinsings in a beaker by themselves. Allow the liquid in the evaporating-dish to become cold, pour upon it a quantity of ordinary strong hydrochloric acid rather larger than the quantity of nitric acid taken at first, evaporate the mixed solution to dryness, and heat the dry residue to render silica in-soluble, in case any silica be present.

Pour water upon the cold residue, and, without filtering the liquor, wash the contents of the dish into the beaker which contains the rinsings of the funnel. Heat the liquid in the beaker nearly to boiling, add to it about 25 c.c. of a strong aqueous solution of ferrous sulphate slightly acidulated with sulphuric acid, and keep the mixture at a temperature near boiling during four or five minutes, in order to destroy the small quantity of nitric acid which may have escaped decomposition in spite of the evaporation with hydrochloric acid.

The ferrous salt seldom or never acts instantaneously, but the reducing action proceeds rapidly and perfectly satisfactorily when once begun. If need be, add more of the ferrous solution, little by little, until the entire contents of the beaker become dark-coloured or almost black, and no more gas is disengaged.

In order to be sure that all the nitric acid has been reduced, it is as well, after the mixture of liquid and solution of ferrous sulphate has been duly heated, to place a drop of the mixture upon porcelain, and test it with ferricyanide of potassium. In general, however, the colouration of the liquor in the beaker, due to the formation of nitrous or hyponitric acid, will be a sufficient indication that the sulphate of iron has done its work. The nitrous fumes quickly disappear from the liquid at a subsequent stage of operations when metallic iron is immersed in the solution.

When enough of the ferrous sulphate has been added, filter the mixed solution into a wide beaker, precipitate the copper in the metallic state upon a sheet of iron in the usual way, and ignite the copper in a porcelain crucible, in a current of hydrogen, before weighing it.

By means of the ferrous salt, the last traces of nitric acid may be got rid of far more quickly, conveniently, and certainly than by the old system of evaporating the pyrites-solution with several successive portions of hydrochloric acid. By treating the pyrites with chlorate of potassium and nitric acid, it is easy to oxidise and dissolve every particle of the sulphur in the mineral, so that no portion of the latter can escape decomposition by becoming enveloped in free sulphur. When aqua regia is used, on the other hand, or a mixture of chlorate of potassium and hydrochloric acid, a certain proportion of sulphur almost invariably remains undissolved, and might easily enclose portions of the mineral, so as to protect them from the solvent action of the acids.

The Mansfeld Processes for Estimating Copper in Ores.

In that portion of Central Germany known as the Mansfeld District, there is found a vein containing metallic ore, which is worked for copper and silver. Generally speaking, however, this ore is extremely variable in value, and since it becomes more and more a matter of immense importance to be able to judge without loss of time of the quantity of metal contained in the ore brought up from various portions of the mines, the want of good means for ascertaining this speedily has long been felt. It need hardly be said that there exist a great many methods for the quantitative estimation of copper in its various combinations; but it is equally true that only very few of these are fit for technical application; it being, moreover, especially desirable that persons not professional assayers or chemists, but superintendents of ordinary intelligence, should be enabled to make the required assays. In the laboratory of the mine owners at Eisleben there has been in use for the poorer copper ores a method of assaying introduced by the late H. Rose, while the raw products of the furnaces were assayed according to a Swedish method. The objection against both these methods, which were executed by properly educated men, was, that for a large number of assays, such as are daily required to be finished there, it took too much time, too much room, and too many hands and apparatus. Rose's method just alluded to is the following:—The finely powdered ore is acted on by aqua regia, to which some sulphuric acid is added; next follow evaporation to dryness, dissolving in acidulated water, separation of the copper by means of sulphuretted hydrogen, and weighing the sulphide of copper after having been ignited and cooled in a current of hydrogen gas. Although the method here

described is a good one, it involves for correctness the condition that no metals precipitable by sulphuretted hydrogen, and non-volatile when ignited in a current of hydrogen, be present. As regards the Mansfeld ores, the absence of such metals has been repeatedly proved; but for all this, it appears that now and then small quantities of molybdenum have affected the correctness of the results.

The Swedish method, however excellent its results, is very cumbrous, and embraces too many different operations to admit of being very readily and thoroughly mastered by many operators. The chief difficulty as regards it is the precipitation of the metallic copper by means of metallic iron: the solution from which it takes place should neither be too hot nor too cold; a large excess of acid also is objectionable. It requires, moreover, a special tact to see when all the copper has been precipitated, since the iron must then be removed from the solution at once, and the acid solution decanted from the copper; in one word, with the greatest possible care, it was not very easy to work the two methods just briefly alluded to with operators who were not specially educated for such work.

Under these circumstances, the directors of the Mansfeld copper mines issued, in May, 1867, an advertisement offering a prize of £45 to anyone who would discover a method of assaying the Mansfeld copper ores which would fulfil certain specified conditions.

To this advertisement sixteen answers were received. Six of the proposed methods were based on the volumetric estimation of copper by means of cyanide of potassium or sulphide of sodium. One proposed method was based upon the estimation of iodine previously set free by means of hyposulphite of sodium; one was by titration with solution of iodine; one by titration with permanganate of potassium; one by titration with sulphocyanide of potassium; one by determination of copper as oxide; two by estimations of copper as sulphide, combined with ignition in current of hydrogen gas; two by a so-called process of dry assay; one by a process by electrolysis.

In order to select from this material, and report upon the best and most suitable plan, a committee of three gentlemen was appointed; two of them practical assayers and copper-smelters, the third the well-known Dr. Bœttger. This committee decided—

(*a*). That any process which included many operations, and consequently took up too much time, is to be excluded.

(*b*). No process is to be admissible which involves the use of varying quantities of ore, since it is impossible to judge by sight of the quality of the Mansfeld ore.

(*c*). Any process is also inadmissible wherein, for the burning off of the bituminous organic matter of the ore, expensive substances, as, for instance, chlorate of potassium, are recommended.

(*d*). Any process is likewise inadmissible wherein the reactions take place with great violence, and may thus induce explosions.

(*e*). Those methods are also inadmissible wherein, for quantities of 5 grammes and more, the treatment with acids and evaporation to dryness after addition of sulphuric acid are necessary.

(*f*). On sanitary grounds, and in reference to the large number of operations and assays daily required, such processes are also inadmissible wherein hyposulphite of sodium is employed so that sulphurous acid is given off; while processes wherein large bulks of sulphuretted hydrogen are used are equally discarded.

(*g*). Methods whereby copper is separated from the earths, oxides of iron, and other metallic oxides, either by ammonia alone, or of carbonate of ammonium, tartaric acid, &c., in addition thereto, are also discarded; because the precipitated oxide of iron or alumina never fails to carry down some copper also; and, also, because oxides like those of zinc, nickel, and cobalt, by remaining in solution, affect the accuracy of the estimation of copper.

(*h*). Those estimations of copper are also discarded whereby it is collected in a spongy state, or as sulphide upon previously dried and weighed filters.

(*i*). The dry assay is also discarded, as, even if it were possible to obtain therewith correct results, it would entail too great expenditure in the consumption of fuel, breaking up of apparatus, crucibles, &c., and the use of various fluxes.

(*k*). Those processes are also discarded which require in the operator too much scientific training.

(*l*). Those which require the aid of assistants are also discarded.

It is clear that many persons who had entered into the competition on this subject could not, owing to the severe conditions, remain in the field. The umpires instituted a large number of assays with divers samples of ores, which had been previously analysed, and the composition of which had been determined with rigorous accuracy, but had not been communicated to them. Their researches proved that, as regards the methods of volumetric estimation, only such deserve any confidence when the copper has been first previously separated in a metallic state, and next re-dissolved; and that then only the titration method with cyanide of potassium is trustworthy.

After a long series of experiments, the umpires decided in favour of Dr. Steinbeck's method in the first place, but were at the same time so satisfied respecting M. C. Luckow's plan, that to that gentleman, who holds the position of chief chemist to the Cologne-Minden Railway Company at Deutz, a premium was also awarded. These two processes are given in the following pages.

Estimation of Copper in the Mansfeld Ores by Dr. Steinbeck's Process.

This method, which entirely answers the imposed conditions, embraces three distinct operations, viz.:—1. The extraction of the copper from the ores; 2. The separation; 3. The quantitative estimation of that metal.

1. **The Extraction of the Copper from the Ore.**—A proof centner, equal to 5 grammes of pulverised ore, is put into a flask, and there is poured over it a quantity of from 40 to 50 c.c. of crude hydrochloric acid, of a specific gravity of 1·16, whereby all carbonates are converted into chlorides, while carbonic acid is expelled. After awhile, there is added to the fluid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a well-arranged sand-bath for half an hour, and the contents only boiled for about fifteen minutes, after which the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or at the most only 0·01 to 0·03 per cent has been left undissolved.

The extraction of the copper from the ore, according to this method, is complete even in the case of the best quality of ore, which contains about 14 per cent of metal; while, at the same time, the very essential condition for the proper and complete separation of the metal, viz., the entire absence of nitric acid, or any of the lower degrees of oxidation of nitrogen, is fully complied with.

2. **Separation of the Copper.**—The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker of about 400 c.c. capacity: in this beaker has been previously placed a rod of metallic zinc, weighing about 50 grammes, and fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate not contain more than from 0·1 to 0·3 per cent of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated fluid, and is, owing chiefly to the complete absence of nitric acid, completely finished in from half to three-quarters of an hour after the beginning of the filtration. If the fluid be tested with sulphuretted hydrogen, no trace even of copper will be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and, in case either

the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must be always employed) has been removed, the spongy metal is repeatedly and carefully washed by decantation with fresh water, which need not be distilled, and care is taken to collect together every particle of the spongy mass.

3. **Quantitative Estimation of the Precipitated Copper.**—To the spongy metallic mass in the beaker, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper is dissolved by the aid of moderate heat, as nitrate of copper; in the event of any small quantity of lead being present, it will of course be contaminated with nitrate of lead.

When copper ores are dealt with which contain above 6 per cent of copper, which may be sufficiently judged from the larger bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are employed for dissolving the spongy metallic mass. The solution thus obtained is left to cool, and next, immediately before titration with cyanide of potassium, mixed with 10 c.c. of normal solution of ammonia, prepared by diluting 1 volume of liquid ammonia, sp. gr. 0·93, with 2 volumes of distilled water.

In the case of ores which yield over 6 per cent of copper, and when a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then divided exactly into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue-coloured solution of oxide of copper in ammonia only contains besides nitrate of ammonium, any lead which might have been dissolved having been precipitated as hydrated oxide of lead, which does not interfere with the titration with cyanide of potassium. The solution of the last-named salt is so arranged, that 1 c.c. thereof exactly indicates 0·005 grm. of copper. Since, for every assay, 5 grms. of ore have been taken, 1 c.c. of the titration fluid is, according to the following proportion,—5 : 0·005 :: 100 : 0·1,—equal to 0·1 per cent of copper; it hence follows that, by multiplying the number of the c.c. of cyanide of potassium solution used to make the blue colour of the copper solution disappear, by 0·1 the percentage of copper contained in the ore is immediately indicated.

As may be imagined, at the laboratory of the mine-owners at Eisleben, such a large number of assays are daily executed that, in this case, there can be no reason to fear a deterioration of the cyanide solution, of which large quantities are used and often fresh made; but for security's sake, the solutions are purposely tested for control at least once every week.

According to the described plan, six assays can be made within 4 hours; and during a working day of from 7½ to 8 hours, twenty assays have been often quite satisfactorily made by the umpires, as well as by the workmen at Eisleben.

Special Observations on this Method.—Dr. Steinbeck considered it necessary to test his method specially, in order to see what influence is exercised thereupon by (1) nitrate of ammonium, (2) caustic ammonia, (3) presence of oxide of lead. The copper used to perform the experiments for this purpose was pure metal, obtained by galvanoplastic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. Five grammes of this metal were placed in a litre flask, and dissolved in 266·6 c.c. of normal nitric acid, the flask and contents gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. exactly. Thirty c.c. of this solution were always applied to test and titrate one and the same solution of cyanide of potassium under all circumstances. When 5 grammes of ore, containing on an average 3 per cent of copper, are taken for assay, that quantity of copper is exactly equal to 0·15 gramme of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 grammes of pure copper (266·6 c.c.), was purposely so taken, as to correspond with the quantity of 8 c.c. of normal nitric acid, which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 30 c.c. of the solution of pure copper.

As regards No. 1 and No. 2 (see above), the influence of double quantities of nitrate of ammonium and free caustic ammonia (the quantity of copper remaining the same), and the action of dilute solution of cyanide of potassium thereupon, will become elucidated by the following facts:—

(*a*). Thirty c.c. of the normal solution of copper, containing exactly 0·15 gramme of copper, were rendered alkaline with 10 c.c. of normal ammonia, and are found to require, for entire decolouration 29·8 c.c. of cyanide of potassium solution; a second experiment, again with 30 c.c. of normal copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide solution. The average of the two experiments is 29·85 c.c.

(*b*). When to 30 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia solution, instead of only 8, whereby the quantity of free ammonia and of nitrate of ammonium is made double what it was in the case of the experiments spoken of under (*a*), there is required of the same cyanide solution 30·3 c.c. to produce decolouration. A repetition of the experiment, under exactly the same conditions, gave 30·4 c.c. of the cyanide solution employed; the average of both experiments is, therefore, 30·35 c.c.

The difference between 30·35 and 29·85 is equal to 0·5 c.c., and that figure is therefore the coefficient of the influence of double quantities; and supposing this to happen with the ores in question, it would only be equivalent to 0·05 per cent of metallic copper. It is hence clear that slight aberrations of from 0·1 to 0·5 c.c. in the measuring out of 8 c.c. of normal nitric acid, used to dissolve the spongy copper, and of 10 c.c. of normal ammonia, in order to render that nitric acid copper solution alkaline, is of no consequence whatever for the technical results to be deduced from the assay; it should, moreover, be borne in mind that the quantities of free ammonia and of nitrate of ammonium in the actual assay of ores, for which always a quantity of 5 grammes of ore is taken, varies according to the richness or poverty of the ores in copper; and the quotation of the following results of experiments prove that the influence of these substances is only very slightly felt in the accuracy of the results:—

Eight c.c. of the normal nitric acid have been found to contain, by means of a series of experiments, 1·353 grammes of anhydrous nitric acid; and this quantity of acid is exactly neutralised by 7·7 c.c. of normal ammonia solution, which contains 0·6515 gramme of oxide of ammonium; and 10 c.c. of the said normal solution contain 0·846 gramme of oxide of ammonium.

One gramme of metallic copper requires, for complete oxidation, 0·2523 gramme of oxygen, and this quantity of oxygen is given off by 0·5676 gramme of anyhydrous nitric acid; while, at the same time, binoxide of nitrogen is disengaged. From these data can be calculated (1) the quantity of nitric acid which becomes decomposed when variable quantities of metallic copper are dissolved therein; (2) what quantity of nitric acid is left to form neutral nitrate of ammonium; and (3) what quantity of free ammonia will be left after a portion of that alkali has been combined with, and therefore neutralised by, oxide of copper; and any remaining free nitric acid.

It is found that the quantitative variations between ores containing 1 per cent or 6 per cent of metal vary very little from the normal quantities exhibited by ores containing 3 per cent of metal. The relation is as 1 : 2; and, for technical purposes, this has been proved not to be a disturbing quantity.

When, however, larger quantities of ammoniacal salts are present in the fluid to be assayed for copper, by means of a titrated solution of cyanide of potassium, and especially when carbonate, sulphate, and, worse still, chloride of ammonium, are simultaneously present, these salts exert a very disturbing influence.

The presence of oxide of lead in the copper solution to be assayed has the effect of producing, on the addition of ammonia, 10 c.c. of normal

ammonia, a milkiness along with the blue tint; but the presence of this oxide does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Dr. Steinbeck, however, purposely made some experiments to test this point, and his results show that neither 50 nor 100 per cent of addition of lead exerts any perceptible influence upon the estimation of copper from its ores, or otherwise, by means of cyanide of potassium. A small quantity of accidentally occurring lead will not, therefore, affect the results, and this the less so as, generally, no ores of both metals occur together wherein both are met in sufficient quantity to make it worth while working the ore for both metals at the same time.

Since it is well known that the presence of zinc very perceptibly influences the action of a solution of cyanide of potassium, when applied to the volumetrical estimation of copper, Dr. Steinbeck considered it necessary to institute some experiments, in order precisely to ascertain with what quantity of zinc present along with copper this influence commences to become perceptible. The solution of zinc applied was made by dissolving the metal in the smallest possible quantity of nitric acid; and 1 c.c. of that solution contained 0·001 gramme of zinc. The results of the experiments show that the presence of zinc does not interfere with the visibility of the end of the reaction, viz., the decolouration of the copper solution. They also prove that a small quantity of zinc, less than 5 per cent of the quantity of copper present, or 0·0075 gramme by weight of zinc, does not at all affect the action of the solution of cyanide of potassium; but when the quantity of zinc increases, a very perceptible effect is seen upon the solution of cyanide; it is therefore necessary to bestow due care while washing the spongy copper, after it has been precipitated by means of zinc from its solution.

Since it has been ascertained that the action of solution of cyanide of potassium in researches of this kind is also affected by an increased temperature of the solution of copper which is to be titrated therewith, it is strictly necessary never to operate with warm ammoniacal solutions of copper, but to suffer the same to cool down to the ordinary temperature of the air of the laboratory.

While 30 c.c. of copper solution, containing 0·15 gramme of copper, and 10 c.c. of normal ammonia solution, required, at the ordinary temperature, 30 c.c. of cyanide solution; the same quantities required, at between 40° to 45° C., 28·8 c.c. of solution of cyanide; and at 45° C., 28·9 c.c. of the same solution, thus proving the injurious effect of warm solutions.

Estimation of Copper in the Mansfeld Ores by M. C. Luckow's Process.

This gentleman has applied to the quantitative estimation of copper a new method, based upon the precipitation of the metal in the metallic state from solutions containing either free sulphuric or nitric acids, by means of a galvanic current.

It is a great advantage of this method, that, while the copper is precipitated, it is simultaneously separated from metals with which it is often found alloyed; some of these, such as tin and antimony, are separated by treatment with nitric acid in an insoluble form, while others, like silver, can easily be removed in the form of chloride. It is, at the same time, another advantage that the state in which the copper is obtained admits of its being accurately weighed and estimated, while a great number of operations, which require much time and various apparatus, are at the same time got rid of.

Although M. Luckow had previously discovered a method of electro-metallic analysis from fluids containing free sulphuric acid, his researches on the same subject, in the case of free nitric acid, belong to a recent period. These researches brought very unexpectedly to light the curious fact that even a weak galvanic current had the power of completely precipitating copper in a pure metallic state from nitric solutions, provided they did not contain more than 0·1 grm. of anhydrous nitric acid to the c.c. (nitric acid of 1·2 sp. gr. contains 0·32 grm. of anhydrous nitric acid to the c.c.), while it was found that the action was, at the same time, more regular, and less dependent upon the power of the current than when free sulphuric acid was present. The following more commonly occurring metals are *not* precipitated by galvanic action from acid solutions:—Zinc, iron, nickel, cobalt, chromium, the metals of the earths and alkalies. The following are precipitated (*a*) in the shape of peroxides, at the positive electrode: completely, lead and manganese; incompletely, silver. When the solution contains traces of manganese, it becomes, in consequence of the formation of a salt of peroxide of manganese, or of permanganic acid, deeply violet-coloured. This very sensitive reaction for manganese also takes place when small quantities of chlorine are present. The presence in the fluid of oxalic, lactic, and tartaric acids, and other readily oxidisable organic substances, and such protoxides as are readily peroxidised—for instance, protoxide of iron—retard the formation of peroxides, as well as the occurrence of the reaction of manganese.

(*b*). Mercury, silver, copper, and bismuth are precipitated at the negative electrode in metallic state. When mercury is present in the solution simultaneously with copper, the former metal is separated before the latter,

in the fluid metallic state. As soon, however, as the precipitation of copper commences, an amalgam of the two metals is formed when mercury is also present. Silver is precipitated almost simultaneously with copper; bismuth only begins to be precipitated after the greater portion of the copper has been separated. A complete separation of silver only ensues when some such substance as tartaric or other similar acid is simultaneously present in the solution. The separation of the three last-named metals, by means of galvanic action, is, therefore, unsuccessful; but, fortunately, there are many other means to accomplish this end completely.

(*c*). Metallic arsenic is only percipitated slowly, and long after the complete separation of copper, if arsenic acid happen to be present. The same remark applies to antimony, since it is well known that small quantities of antimonic acid are soluble in nitric acid.

The operations, according to Luckow's plan, are—1. Roasting the ore; 2. Solution of the roasted product; 3. Precipitation of the copper; 4. Weighing the copper.

1. **Roasting the Ore.**—Care should be taken to obtain a finely-ground average sample of the ore. Then weigh off, in small porcelain capsules previously counterpoised, quantities of from 1 to 3 grms.; these quantities are then placed on the inverted lid of an iron crucible, on the inner surface of which the powdered ore is heated over the flame of a Bunsen gas-burner. The powder may be carefully stirred up with a platinum wire, to promote the access of air during the roasting; the ignition of bituminous matter and sulphur will be ended in about seven minutes. Ores which do not contain bitumen at all need not be roasted.

It has been already stated that in the case of poor copper ores (and those of the Mansfeld district are generally so), the quantities to be weighed off for assay should not vary according to a presumed percentage of copper. Two grms. are therefore taken, and, instead of roasting the ore on the lid of an iron crucible, small porcelain crucibles are applied for that purpose.

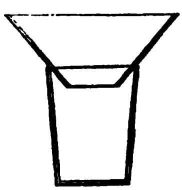
2. **Solution of the Roasted Product.**—The iron lid is suffered to cool, the roasted powder placed on a piece of glazed paper, and any powder adhering to the lid is removed by means of a camel's-hair brush on to the paper. The powder is next transferred to small beaker glasses, and about 2 or 3 c.c. of nitric acid, of 1·2 specific gravity, are added, along with about 10 to 15 drops of concentrated sulphuric acid. The beakers are then placed on a sand-bath, and moderately heated, at first; but when the contents have nearly become dry, the heat is increased, so as to evaporate and expel all sulphuric acid. The beakers should be covered with perforated watch-glasses. This operation requires from about three-quarters of an

hour to one hour. The addition of sulphuric acid is made in order to increase the oxidising action of the nitric acid, and also to convert any lime which may happen to be present in the ore into a difficultly soluble salt. It is very useful, also, to add from 10 to 20 drops of hydrochloric acid to the mixture of the two acids just alluded to, since the rapidity of the evaporation is thereby increased, and the occasional spirting about of the fluid is lessened.

The process just described may be modified, first by the use of porcelain capsules, the contents of which are easily transferred to beakers with flat bottoms, and not higher than about 2 inches altogether. It is better, also, to use a sulphuric acid, prepared with equal bulks of concentrated acid and water, and to measure off 4 c.c. for each assay; while for each assay, moreover, 6 c.c. of nitric acid and about 25 drops of hydrochloric acid are taken. Instead of covering the beaker with a perforated watch-glass, the upper part of a funnel is used, as represented in Fig. 2; with this arrangement the sulphuric acid evaporates far more readily, and loss by spirting is prevented. The beaker is heated on a well-arranged sand-bath.

3. **Precipitation of the Copper.**—As soon as the beaker after removal from the sand-bath has become quite cool, the funnel which has been used

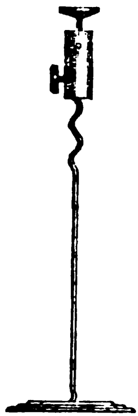
FIG. 2.



as a cover is washed on both sides, inner and outer, with nitric acid of 1·2 sp. gr., diluted with six times its bulk of pure water; the sides of the beaker are next likewise washed, and it is then filled to about half its height with the same acid. A few drops of a concentrated solution of tartaric acid are added (this acid is best kept in solution in open vessels, only slightly covered with a piece of paper); this having been done, the wire spiral, represented in Fig. 3, is carefully placed in the beaker. This spiral consists of a piece of platinum wire, about 1-12th of an inch thick, and 7½ inches long, two-thirds of its length being so wound that the straight end of the wire projects as if it were the axis of the centre of the spiral. The convolutions of the spiral are so large that they touch the sides of the beaker, while the straight portion just touches the centre of the bottom of the vessel.

When the heating has been carefully attended to, the acid fluid added to the contents of the beaker, after evaporation to dryness, will generally be quite clear; if it happens to be turbid, 1 or 2 c.c. of a concentrated solution of nitrate of barium may be added, and the thorough mixing of this saline solution with the acid contents of the beaker promoted, by gently moving up and down the platinum spiral just alluded to, and allowing the fluid to rest for a few minutes after. The copper present in the mass left at the bottom of the beaker gradually dissolves, and it is not

FIG. 3.



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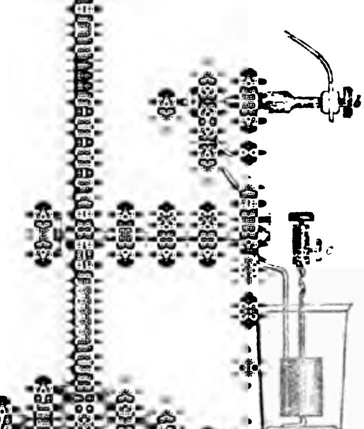

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the platinum wire spiral bubbles of gas escape, which facilitate, to some extent, the solution of the oxide of copper in the dilute acid.

In order to ascertain whether the whole quantity of the copper has been precipitated, some more dilute nitric acid is added to the fluid in the beaker glass. If, in ten minutes after this, no more metallic copper is separated on the clean portions of the platinum foil, the operation is finished.

It must be here observed that continued practice has proved that the addition of a concentrated solution of nitrate of barium acts injuriously on the process, as the metallic copper, which becomes separated, gets mixed with some insoluble sulphate of barium, which increases the weight of the substance to be weighed.

The time occupied by the complete precipitation of the metal varies according to the force of the galvanic current. It takes from three to even eight hours. In order to make this point certain, all test assays are left for eight hours consecutively, to the action of the galvanic current, experience having proved that, after that lapse of time, even with a weak current, the precipitation was so complete that all chemical reagents for detecting the presence of copper failed to discover the most minute trace of that metal.

4. Weighing the Copper. — The platinum cylinder to which the copper adheres, and the platinum wire spiral, are disconnected from the galvanic apparatus, the platinum cylinder carefully removed from the beaker and immediately plunged into a beaker filled with fresh cold water, and rinsed therein; next washed with alcohol, by means of a washing bottle, and then dried in a drying apparatus, and weighed after cooling. Since the platinum cylinder has been very accurately weighed *before* the experiment, its increase in weight will, of course, be that of the copper obtained.

The process here described has been somewhat modified and greatly improved upon at Eisleben, where it is in constant use, by the employment of a series of galvanic elements. It is, in the first place, found better not to disconnect the galvanic current while the copper is yet in contact with acid, so that, instead thereof, the acid fluid in the beaker is replaced by turning in a stream of water, and suffering the same to run over the sides of the beaker, and to be received into a proper vessel to hold it. In this manner all the acid is displaced, without risk of any very small quantity of copper becoming acted upon by the acid during the brief period elapsing between the disconnecting of the galvanic current and the removal from the beaker of the platinum cylinder and spiral wire. These parts, on being removed, are carefully washed, first with boiling water, next with alcohol, and then dried at a temperature of about the boiling point of water. The cylinder is then weighed, the copper coating is removed by means of nitric acid; the platinum is next washed in water, dried, and again weighed.

There are in use at Eisleben nine galvanic batteries (lead and zinc elements); these yield eighteen assays ready for weighing in twenty-four hours; and it would not be difficult for the person there employed to work with twelve batteries each of three elements. The results obtained are highly satisfactory. The following observations may be made in reference to this method:—

(*a*). The quantity of ore taken for trial is 2 grammes; this is found sufficient, while it consumes less acid.

(*b*). The evaporation of the acid is carried on to complete dryness on the sand-bath. Spirting of the fluid is easily prevented.

When the copper has been precipitated properly it will show its peculiar colour on the surface, and the good success of the operation may also be judged from the fact that no saline matter adheres to the platinum; the complete absence of this saline matter has been found to be evidence of perfect removal of the copper from the fluid.

The process just described is especially applicable for rather poor ores, such as do not contain above 7 or 8 per cent of copper. Each assay, from beginning to end, takes ten hours for complete analysis; but it is evident that the greater portion of this period does not give active employment to the assayer. The expense of working this process, after the apparatus has been once purchased, is very small. The process may also be applied to analyse richer ores, and also alloys of copper, with some slight modifications which will readily suggest themselves.

Detection of Minute Traces of Copper in Iron Pyrites and other Bodies.

Although an exceedingly small percentage of copper may be detected in blowpipe experiments by the reducing process, as well as by the azure-blue colouration of the flame when the test-matter is moistened with hydrochloric acid, these methods fail in certain extreme cases to give satisfactory results. It often happens that veins of iron pyrites lead at greater depths to copper pyrites. In this case, the iron pyrites will almost invariably hold minute traces of copper. Hence the desirability, on exploring expeditions more especially, of some ready test by which, without the necessity of employing acids or other bulky and difficultly portable reagents, these traces of copper may be detected. The following simple method is due to Dr. E. Chapman, Professor of Mineralogy and Geology, Toronto, and will be found to answer the purpose:—The test-substance, in powder, must first be roasted on charcoal, or, better, on a fragment of porcelain * in order to drive off the

* In the roasting of metallic sulphides, &c., small fragments of Berlin or Meissen porcelain, such as result from the breakage of crucibles and other vessels of that material, may conveniently be used. The test-substance is crushed to powder, moistened slightly,

sulphur. A small portion of the roasted ore is then fused on platinum wire with phosphor salt, and some bisulphate of potassium is to be added to the glass (without this being removed from the wire) in two or three successive portions, or until the glass becomes more or less saturated. This effected, the bead is to be shaken off the platinum loop into a small capsule, and treated with boiling water, by which either the whole or the greater part will be dissolved; and the solution is finally to be tested with a small fragment of ferrocyanide of potassium. If copper be present in more than traces, this reagent, it is well known, will produce a deep red precipitate. If the copper be present in smaller quantity—that is, in exceedingly minute traces—the precipitate will be brown or brownish-black; and if copper be entirely absent, the precipitate will be blue or green—assuming, of course, that iron pyrites or some other ferruginous substance is operated upon. In this experiment the preliminary fusion with phosphor salt greatly facilitates the after solution of the substance in bisulphate of potassium. In some instances, indeed, no solution takes place if this preliminary treatment with phosphor salt be omitted.

Another very delicate method of detecting traces of copper before the blowpipe by the employment of chloride of silver will be found in a subsequent chapter.

Estimation of Suboxide of Copper in Metallic Copper.

When dilute sulphuric acid acts upon suboxide of copper in the presence of nitrate of silver, the suboxide is split up into metallic copper and oxide of copper; the latter becomes dissolved as sulphate, while the metallic copper takes the place of the silver of the nitrate of that metal. In order to apply this reaction for analytical purposes, M. C. Aubel takes 0·5 grm. of the copper to be tested, previously reduced, by proper mechanical means, to powder or filings; and adds to it 1·3 grm. of solid nitrate of silver mixed in a mortar with 10 c.c. of dilute sulphuric acid. The decomposition sets in at once, and is entirely complete after two hours' time; water is then added, the metallic silver is collected on a filter, well washed, and, after having been dried, is weighed. From its weight the amount of suboxide which was present is easily calculated.

Separation of Copper from Mercury.

Copper and mercury are conveniently separated by the addition of phosphorous acid to the dilute hydrochloric solution of the two metals.

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and spread over the surface of the porcelain; and when the operation is finished, the powder is easily scraped off by the point of a knife-blade or small steel spatula. In roasting operations, rarely more than a dull red heat is required; but these porcelain fragments may be rendered white-hot, if such be necessary, without risk of fracture.

On standing for some time in the cold, the mercury is precipitated in the form of protochloride. The filtrate is heated to ebullition, and the oxide of copper precipitated by caustic potash.

Separation of Copper from Silver.

The ordinary methods of separating copper from silver are too simple to require mention here. It may happen, however, that a rapid and approximate separation of nitrates of silver and copper is wanted without resorting to the process of precipitating the silver as metal or as chloride. Under these circumstances the following process will be useful. It is supposed that the object is to prepare nitrate of silver from silver coins which contain a large percentage of copper. The alloy is dissolved in nitric acid; the solution is filtered if necessary, and evaporated until it has the consistency of a thickish oil; when this point is reached there is added to the solution very concentrated nitric acid free from hydrochloric acid. By this proceeding all the nitrate of silver is precipitated, while nitrate of copper remains in solution. One part of the concentrated metallic solution requires from three to four parts of nitric acid for the complete precipitation of the nitrate of silver; the more concentrated the nitric acid is the better, but acid of 1·250 sp. gr. answers the purpose. The solution of copper is decanted off, and the nitrate of silver washed with nitric acid.

Separation of Copper from Nickel or Cobalt.

Obtain the metals in a slightly acid solution, and add sulphurous acid till the copper is entirely reduced to the state of sub-salt. Then precipitate with sulphocyanide of potassium, and after allowing the precipitate to digest in the liquid for a short time, filter off the white subsulphocyanide of copper.

The ordinary process for separating copper from nickel, founded on the precipitation of copper by sulphuretted hydrogen, leaves much to be desired on account of the facility with which sulphide of copper after washing passes to the state of sulphate; and also because copper, during precipitation, always carries down with it considerable quantities of nickel, which passes to the state of sulphide in the precipitate. M. Dewilde has worked out a method of separating these metals based upon the property possessed by glucose of precipitating copper as a suboxide, when that metal exists in the form of tartrate dissolved by the aid of caustic potash. His process is as follows:—

Dissolve about 2 grms. of the alloy in hydrochloric acid containing a little nitric acid; evaporate off the excess of acid, and dissolve the mixed chlorides in about 50 grms. of water. To the solution add about 4 grms. of cream of tartar. Heat slightly to facilitate solution, and add gradually a solution of

caustic potash in alcohol. The first addition of alkali precipitates the oxides of copper and nickel in the state of hydrates, but an excess of potash re-dissolves the whole, the tartrates of copper and nickel being soluble in caustic potash. A blue solution is thus obtained, which after cooling is treated by a solution of pure glucose or inverted sugar, and boiled for one or two minutes. The copper is precipitated as a beautiful red suboxide sinking quickly to the bottom of the vessel; if, however, the glucose is added to a warm solution, the copper is precipitated in flakes which it is difficult to wash. The completion of the precipitation is ascertained by adding a further quantity of the glucose solution.

The precipitated suboxide of copper is washed, dried, and ignited. It may be heated with nitric acid, and protoxide of copper obtained by igniting the nitrate so obtained.

The filtrate containing the nickel is evaporated to dryness, the residue calcined, and then washed to remove the carbonate of potassium. As the incineration can never be complete, on account of the presence of this salt, the operation is to be repeated. The residue, consisting chiefly of oxide of nickel, is dissolved in aqua regia, and the hydrated oxide of nickel precipitated from the solution by caustic potash. It is very difficult, if not impossible, to wash this very voluminous oxide, so the best plan is to wash incompletely, dry, and slightly calcine the oxide; after grinding this in an agate mortar, it is easily freed from the last trace of potash by washing in warm water. The oxide thus obtained is reduced in a platinum crucible in an atmosphere of hydrogen.

This process is in use in the Belgian mint, where copper and nickel alloys are used for coinage.

Separation of Copper from Zinc.

The solution of copper and zinc must contain no other metal which forms an insoluble iodide. Add sulphurous acid to the solution, and then, after gentle heating, iodide of potassium, until the supernatant liquid has lost its blue colour and a precipitate is no longer formed. There should be a slight excess of sulphurous acid the whole time. The subiodide of copper being very dense deposits readily, especially on warming, like chloride of silver. Heat to the boiling point, and collect on a weighed filter. The precipitate, washed with warm water, is dried at 120° and weighed. All the zinc will be in the solution.

Another very perfect method of separating copper from zinc consists in dissolving in nitric acid, evaporating to dryness, and heating to redness, so as to leave a mixture of oxides of copper and zinc. Finely powder these oxides, and introduce them by means of a platinum boat into a small, light glass tube, furnished with a good cork. The weight of the boat, tube, and

cork being already known, another weighing, after having heated them to redness in a current of air, gives the weight of the mixture of oxides. The boat is then introduced into a combustion-tube, and a current of dry hydrogen is passed over, whilst heat is applied sufficient to reduce the oxide of copper. When the boat and its contents cease to lose weight, remove them to the small corked tube, allow to cool, and weigh. The contents of the boat will now consist of oxide of zinc and metallic copper, and from the amount of oxygen lost the quantity of copper present may be ascertained with accuracy. (Supposing no impurities are present, the loss, multiplied by 5, gives very nearly the amount of copper present, and if the object has been merely to ascertain the composition of a sample of brass, the operation may be terminated; otherwise, it may be concluded as follows). Prepare dilute sulphuric acid, perfectly freed from nitroxygen compounds, by distillation over sulphate of ammonium, heat the acid to completely free it from air, and pour it over the mixture of oxide of zinc and copper in a small stoppered flask. The oxide of zinc will be dissolved, whilst the metallic copper will remain intact. After allowing the mixture to rest for some hours, decant and wash the copper several times in boiled water. The solution contains all the zinc; evaporate to dryness, heat to about 400° C., and weigh as anhydrous sulphate.

CHAPTER VIII.

CADMIUM, LEAD, THALLIUM, INDIUM, BISMUTH.

CADMIUM.

Estimation of Cadmium.

A VERY accurate and rapid process of estimating cadmium is to make use of the reaction worked out by Leison.

Obtain the metal in the form of a strong aqueous solution as neutral as possible; add oxalic acid in excess, and then a large quantity of strong alcohol. The resulting oxalate is beautifully crystalline, and the precipitation is so complete that sulphuretted hydrogen gives a scarcely perceptible yellowish tinge in the filtrate. Wash the oxalate by Bunsen's method, and dry at 110° C., until every trace of alcohol is expelled. Then pierce the filter with a glass rod, and wash the oxalate of cadmium into a flask with hot dilute hydrochloric acid. A few c.c. of strong sulphuric acid are then added, and the hot solution is titrated with permanganate of potassium. The results are very accurate. For further details on this method of analysis see p. 63.

Separation of Cadmium from Copper.

Sulphide of cadmium dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on sulphide of copper. On precipitating by sulphuretted hydrogen a solution containing not more than 1 milligramme of cadmium mixed with 1000 milligrammes of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part concentrated acid and 5 parts of water), a colourless filtrate is obtained, in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow sulphide of cadmium. Another solution of the same composition was mixed with an excess of cyanide of potassium and treated with sulphuretted hydrogen gas. A distinct yellow colouration was observed: a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in cyanide of potassium also gives rise to a yellow colouration when submitted to the action of sulphuretted hydrogen.

Another method for the separation of cadmium from copper, due to Wöhler, is as follows:—Well wash the precipitated sulphides, and then

dissolve them in hydrochloric acid, to which is added chlorate of potassium. Precipitate the solution by an excess of potash, and dissolve the precipitate in hydrocyanic acid. This will form a solution of double cyanides, from which sulphuretted hydrogen precipitates the cadmium, but not the copper.

Another plan is to add to the solution of the two metals a considerable excess of tartaric acid, then a solution of caustic soda to alkaline reaction. Now dilute considerably, and boil for some hours; the cadmium will be deposited. The filtrate containing the copper is then oxidised with aqua regia and precipitated with caustic potash.

Copper and cadmium may also be separated by precipitating the former with sulphocyanide of potassium, after having first reduced it with sulphurous acid.

Separation of Cadmium from Mercury.

To the solution of the mixed metals add excess of hydrochloric acid and then phosphorous acid. This precipitates the mercury in the form of protochloride. Filter off, and to the filtrate add carbonate of sodium, which will precipitate the cadmium as white carbonate. This is washed, dried, and converted by ignition into brown oxide. Care must be taken to remove as much of the precipitate from the filter as possible before calcining it.

Separation of Cadmium from Zinc.

Add a considerable excess of tartaric acid to the solution containing these two metals. Then add solution of caustic soda until the reaction is decidedly alkaline, and after dilution with much water keep the solution in a state of ebullition for several hours. Only the cadmium is deposited. The zinc may be separated from the filtrate by sulphide of ammonium.

LEAD.

Preparation of Pure Lead.

As in the case of silver, the most valuable of our knowledge on the subject of the purification of metallic lead is due to the researches of Professor Stas on the relations existing between atomic weights. The preparation of pure lead offers even more difficulties than that of pure silver.

In the following pages are given those processes which yielded the best results.

Preparation of Lead by Reducing the Carbonate with Cyanide of Potassium.—Commercial acetate of lead was dissolved in warm water, contained in a large leaden digester, and kept at a temperature of 40° to 50° in contact with very thin sheets of lead until all the copper and silver were precipitated. The solution was then filtered and poured into nearly

boiling water, strongly acidulated with sulphuric acid. The sulphate of lead was washed by decantation until the washing waters contained no trace of sulphuric acid. The salt was then transformed into carbonate by means of a mixture of sesquicarbonate of ammonium and solution of ammonia; for this it is only needful to diffuse it in the water containing the alkaline salt, an effervescence takes place, which lasts as long as there remains sulphate of lead undecomposed. At this point the solution of sulphate of ammonium and the excess of carbonate of ammonium is decanted, and the precipitate washed with pure water as long as the washing waters contain sulphate in solution.

The carbonate of lead thus formed dissolves entirely in dilute nitric acid. It is perfectly free from foreign metals, except traces of iron, which adhere to the sulphate of lead in spite of the excess of sulphuric acid employed. To separate the iron, transform a portion of this carbonate of lead into oxide, by heating it carefully in a platinum vessel. Another portion is dissolved in dilute nitric acid, taking the precaution to leave some of the carbonate undissolved. The solution of nitrate is heated to ebullition and the oxide of lead then gradually added to it. The oxide in dissolving precipitates traces of iron. The liquid is filtered and an excess of sesquicarbonate of ammonium poured into it. In the carbonate of lead thus obtained it is impossible to discover the slightest trace of foreign metal. It is this carbonate which is converted into metallic lead. To effect this, after having dried it, project it, by small quantities at a time, into pure fused cyanide of potassium. As this reduction ought to be effected in a white, unglazed, porcelain crucible, which is very liable to break, recourse may be had to the same plan which was used in the reduction of silver from its chloride, and in the fusion of the pure metal (p. 166)—that is to say, fix the porcelain crucible in the centre of another larger one, interposing between them calcined pipe-clay, which has been reduced to powder, cementing the whole together by the addition of five per cent of fused and powdered borax.

The lead obtained by the first operation is heated a second time with pure cyanide of potassium until it presents at the bottom of the cyanide a surface as convex and brilliant as pure mercury. When it is somewhat cool, cast it in a polished ingot-mould of cast-steel.

When the lead contains the slightest trace of oxide or sulphide it does not present a convex surface when it is fused.

Pure lead is much whiter and more soft than the ordinary metal. It appears to tarnish very rapidly when exposed to the air.

Preparation of Lead by Reducing the Carbonate by Black Flux.—Instead of reducing the carbonate of lead by cyanide of potassium, black flux obtained by carbonising purified Seignette salt may be employed. To

entirely deprive this salt of foreign metals, first pass a current of hydrosulphuric acid through its boiling solution; then pour in a few drops of sulphide of sodium solution. The coloured solution, left to itself for fifteen days in a well-stoppered bottle, becomes completely decolourised by depositing the metallic sulphides. The decanted solution is agitated with tartate of lead as long as it contains the slightest trace of sulphide of sodium. Before calcining the Seignette salt, it should always be tested to see that it contains neither sulphide, sulphate, nor foreign metals.

The carbonate of lead mixed with the pulverised black flux is reduced by the action of heat. The temperature necessary for the fusion of the alkali being tolerably high, there are almost always a certain quantity of alkaline metals reduced, which alloy with the lead. To remove these metals, heat the lead for some time in contact with the air, continually stirring the metallic bath with a rod of pipe-clay. When a certain quantity of the lead has been thus oxidised, pour on the mass fused cyanide of potassium, and heat the whole until a great portion of the cyanide is volatilised. The lead is then allowed to cool to near its point of solidification, and then run into an ingot-mould of polished steel.

Preparation of Lead by Reducing the Chloride.—Treat with an excess of dilute hydrochloric acid the carbonate of lead prepared by the action of sesquicarbonate of ammonium upon the sulphate of lead. The minute traces of iron contained in the carbonate remain dissolved in the excess of hydrochloric acid. Two different plans may be used to reduce the chloride. One consists in mixing it with two-thirds of its weight of pure carbonate of sodium and projecting the intimate mixture into fused cyanide of potassium. The metallic lead produced is poured into another crucible with a fresh quantity of pure fused cyanide of potassium. It is there kept at a high temperature and continually agitated until the surface, flat and dull as it is at first, becomes strongly convex and brilliant. When sufficiently cool it is poured into an ingot-mould and kept away from moist air.

The other plan of reducing the chloride consists in heating an intimate mixture of it with carbonate of sodium and black flux. The resulting lead is fused and agitated for some time in contact with air, and then heated with cyanide to remove the last traces of oxide.

Estimation of Lead by Precipitation in the Metallic State.

To estimate lead by this method, M. F. Stolba treats both soluble and insoluble lead combinations with zinc in the presence of water acidulated from time to time with hydrochloric acid; the reduction is effected at the temperature of the water-bath in a platinum capsule; the lead is deposited partly on the sides of the capsule and partly on the zinc, whence it is

easily dislodged. When the reduction is complete, which is easily discerned by a clean surface of the zinc remaining brilliant in the liquid, decant and wash the spongy deposit of lead with water. As pure water might oxidise and dissolve small quantities of lead, an addition of a drop of sulphuric acid is advisable. After washing, dry the lead first in a water-bath, then at about 200° C. Its exact weight cannot then be ascertained because it has undergone a partial oxidation. After weighing it the amount of oxygen absorbed must be ascertained, which may be done by treating the lead with a weak standard solution of nitric acid. Wash the lead from dissolved oxide, and to the acid solution add a standard alkaline solution until it begins to produce turbidity. The quantity of oxide of lead is given by the difference in the standard of the nitric acid before and after its action on the lead.

Precipitation of Lead as Sulphate.

The estimation of lead in the state of sulphate, by means of sulphuric acid and evaporating to dryness, insures accuracy, but the process requires constant attention. Towards the end of the analysis the evaporation exposes it to loss by projection; moreover, if the liquids contain iron, the sulphate of lead is often contaminated with the slightly soluble ferric sulphate. The solubility of sulphate of lead, even in water, is well known, as the following experiment shows:—Precipitate one equivalent of nitrate of lead by two equivalents of sulphuric acid diluted largely with water; then wash during several days, and long after the washings have ceased to redden litmus-paper, they will still become slightly turbid by nitrate of barium and sulphide of ammonium.

The use of soluble sulphates, suggested by various authors, M. Levol has shown is not to be recommended.

The first impression was, that the principal inconvenience arose from the incomplete insolubility of sulphate of lead, and that, consequently, the employment of alkaline sulphates would produce but imperfect results. But it appears that, under these circumstances, there is an overweight in precipitating lead by sulphate of potassium. If, in fact, liquids much charged with nitrate of lead and sulphate of potassium or sodium in excess are put in contact, precipitates are obtained the weight of which considerably exceeds that of the sulphate of lead corresponding to the weight of nitrate; and it is with difficulty that they are reduced to this weight by washing.

From careful analyses, it appears that there are formed by the wet way, under certain conditions, double sulphates of lead and potassium, or sodium, and in a paper published in 1825 by Tromsdorff, it is pointed out that the potassic salt is obtainable by the precipitation of acetate of lead by sulphate of potassium. He also adds that by boiling this salt with a large quantity of water, the proportion of sulphate of potassium which it contains gradually diminishes.

It is only under particular conditions of concentration of the liquids that these salts can be formed, but, on the whole, experience shows that alkaline sulphates should not be employed in the estimation of lead in the state of sulphate, if the precipitate is weighed, partly because of the danger about to be described, and partly because of the fear of loss of sulphate of lead by the numerous washings necessitated by the decomposition of the double salts by water.

Estimation of Lead as Carbonate.

In face of the difficulties to be encountered in estimating lead with great accuracy, it appears advisable that it should be determined in the state of carbonate, and for that purpose ordinary carbonate of ammonium, to which is added caustic ammonia, should be used. The object of this addition is to avoid the employment of too large a volume of solution of carbonate of ammonium, a salt not very soluble in water. Ammonia forms, with nitrate of lead, for instance, a very incomplete precipitate, the composition of which is represented by $2(6PbO,NO_5)+3HO$. It would not, then, be prudent to divide the operation into two—that is to say, to employ ammonia first to saturate the liquid—and, consequently, it should not be poured in until it has been charged with carbonate of ammonium, which it dissolves abundantly and easily. The precipitate separates perfectly from the liquid, is easily collected and dried on a filter. The deposition of the precipitate is completed in about 24 hours, especially under the influence of gentle heat. Two or three 1000ths of lead can be estimated by this process.

The precipitate, which is the anhydrous protocarbonate, is deposited on a small double filter, each one of the same weight.

If, as frequently happens in analysing metallic substances, the colour, which should be pure white, is yellowish, it is owing to the presence of iron, which is easily got rid of by washing the filter with water acidulated with sulphuric acid after weighing.

If there is reason to suspect the presence of bismuth, treat a small quantity of the weighed precipitate by a little nitric acid. A few drops of iodide of potassium in the liquid will detect the presence of bismuth by the forming of a brown precipitate, or yellow-brown if there is bismuth and lead. The latter metal, when present alone, gives a pure yellow precipitate. (See also Separation of Bismuth from Lead).

Precipitation of Lead by Oxalic Acid.

It has already been stated that in estimating lead by carbonate of ammonium, in presence of an excess of ammonia, two or three 1000ths of this metal can be determined. By operating, under the same conditions, with oxalic acid, it is impossible to determine it to less than 1 per cent. It

has been observed that the precipitation of lead by oxalic acid should be effected in neutral solutions; but this necessity but ill agrees with the most ordinary instances of the analysis of metallic substances, where the presence of an excess of ammonia is indispensable for maintaining in solution certain substances from which the lead requires to be separated.

Volumetric Estimation of Lead.

M. Graeger determines lead with ferrocyanide of potassium.

Ferrocyanide of lead is almost insoluble in acids, and its precipitation is easy. The author employs a standard solution of ferrocyanide of potassium; when all the lead is precipitated, the liquid colours ferric salts blue, which may be tested in one drop of it. An excess of ferrocyanide may be added, and determined in the filtered liquid by permanganate of potassium. As a control, the ferrocyanide of lead may be suspended in water, and titrated by permanganate.

Detection and Estimation of Small Quantities of Lead in the Presence of Other Metals.

The separation of lead from its solutions and from other metals by means of chromate of potassium, does not appear to have attracted the attention of analytical chemists to the extent which it merits, judging from the published special methods of analysis which include the determination or detection of that metal.

There are frequent instances in which the chromate of potassium offers considerable advantage as a precipitant of lead over hydrosulphuric or sulphuric acids, the two reagents in general use, more particularly for the detection of minute quantities. The efficiency of this reagent, is moreover, much increased by the circumstance that chromate of lead is all but insoluble in acetic acid. It is, indeed, one of the most insoluble of the lead salts, and has, therefore, claim to superiority over the more soluble sulphate; whilst the scarcity of insoluble chromates renders chromate of potassium valuable for effecting the separation of lead from other metals in cases where the reagents referred to are inapplicable. The precipitation of lead in the presence of copper, for example, is more readily effected by the addition of bichromate of potassium to an acetic solution; a trace of lead which would otherwise escape detection is rendered evident after a time by the deposition of the characteristic yellow precipitate.

Bichromate of potassium in the presence of free acetic acid is also applicable as a means of separating small quantities of lead from zinc (*i.e.*, in the analysis of the spelters in commerce). The precipitation of lead by hydrosulphuric acid from the hydrochloric solution is at times anything but satisfactory, the solubility of the sulphide of lead in the excess of

hydrochloric acid which must be employed to prevent the precipitation of the zinc is sufficient to lead frequently to the belief that lead is absent when it really exists in the spelter to a very appreciable amount. (It may be observed that this liability to error, in the use of hydrosulphuric acid, is not nearly so great when nitric acid is employed).

If much bismuth be present in the substance under examination, some chromate of bismuth will be precipitated, together with the lead. In such instances the separation of the two metals must be effected by a special method.

The chromate of lead, when freshly precipitated from a cold solution, is sometimes difficult to separate perfectly from the liquid by filtration; this is not the case, however, if the precipitate is allowed to stand for some time, or if it is produced in a hot solution.

The most accurate way of determining the weight of minute quantities of lead precipitated as chromate is to convert the metal finally into sulphate. For this purpose the chromate is dissolved in a little hot dilute hydrochloric acid; a small crystal of tartaric acid is added, and the solution, rendered alkaline by ammonia, is treated with hydrosulphuric acid, or mixed with a few drops of sulphide of ammonium. The sulphide of lead thus obtained is washed and converted into sulphate by the usual method.

Volumetric Estimation of Lead by Precipitation as Chromate.

Some years ago Dr. H. Schwarz published a process for the volumetric estimation of lead which consisted in precipitating a lead solution (acidulated with nitric acid) by means of an excess of bichromate of potassium; the precipitate when subsided had to be washed and filtered, and precipitate and filter placed in a freshly-prepared standard solution of protochloride of iron. Decomposition took place, the chromic acid was reduced to the state of oxide, and the lead converted into and dissolved as chloride. When filtered and washed, the remaining undecomposed protochloride of iron was estimated by permanganate of potassium, and from the difference between the remaining and original amount of iron the quantity of chromic acid was calculated, and in this way the amount of lead ascertained. This process, while it gives accurate results, requires, like that devised by Hempel, two filtrations and washings.

The following process is more simple:—Dissolve 14·730 grms. of pure bichromate of potassium in sufficient water to form one litre. One cubic centimetre of this solution precipitates 0·0207 grm. of lead.

In the analysis of metallic lead, a certain quantity should be dissolved in a minimum of nitric acid, the solution diluted with water, carefully neutralised with ammonia or carbonate of sodium, an excess of acetate of sodium added, and the solution precipitated by the bichromate of potassium

solution. When the precipitation approaches its end, or when the precipitate commences readily to subside, some drops of a neutral solution of nitrate of silver are spread out on a porcelain plate, and the chromate of potassium solution only added by two or three drops at a time to the liquid under examination: after each addition the whole is well stirred, allowed to subside, and the silver solution on the plate touched with a drop of the clear supernatant liquor. As soon as the bichromate of potassium is in excess the two drops form a red colour, while the precipitated chromate of lead has no effect on the silver test, but simply floats on the top as a yellow precipitate. Should the solution assume a yellow colour before the silver reaction has commenced, it would indicate that not sufficient acetate of sodium had been added in the first instance, and it would be necessary to add this now, and also a c.c. of a normal lead solution, containing 0·0207 of lead as nitrate. The slight turbidity which first takes place soon goes off, and the operation may be proceeded with as before. One c.c. must, of course, in this case, be deducted from the amount of chrome solution on account of the extra addition of lead.

Of all foreign metals bismuth alone seems to interfere with the reaction; it behaves very like lead with chromic acid, and, if present, necessitates a different mode of proceeding. Tin and antimony are converted into insoluble oxides during the solution of the lead in nitric acid. Arsenious acid offers no difficulties, but arseniate of lead is insoluble in an acetic solution, and is only partly decomposed by bichromate of potassium, consequently its removal becomes necessary. Gold and platinum are insoluble in nitric acid.

The presence of silver is of no great importance; during the operation the lead is first thrown down as a yellow precipitate, and afterwards the precipitation of the silver takes place, giving the red reaction similar to the silver test always resorted to. It may, however, be separated from the lead solution by means of chloride of sodium, and the chloride of silver either filtered off, or in case not much excess of chloride of sodium has been used, left in the solution, and the lead estimated as usual. Chloride of lead is tolerably soluble in hot water, and chromate of lead is not decomposed by chloride of sodium, although this salt decomposes chromate of silver.

The higher oxide of mercury is not precipitated by bichromate of potassium, not even in an acetic solution, while the lower oxide is; and, as it is difficult to peroxidise all the mercury when amalgamated with lead, even by long-continued boiling in nitric acid, it becomes necessary to evaporate and calcine the residue till all the mercury is volatilised. To obviate the formation of peroxide of lead, the calcined residue must be moistened with a few drops of oxalic acid, and again dried and carefully calcined and dissolved in acetic acid; after this, the lead may be estimated as usual. To avoid the above calcinations the mercury may be precipitated from the

nitric acid solution by means of hydrochloric acid, and the calomel boiled till converted into the higher chloride.

Copper, cadmium, zinc, iron, and cobalt do not in the least interfere with the reaction, provided the iron is peroxidised. Of the different acids, hydrochloric acid somewhat disturbs the last silver reaction, but by using larger drops, and allowing the reaction of chloride of silver to go off, the usual chromate of silver reaction is obtained.

Sulphate of lead has first to be converted into the state of carbonate, by boiling with carbonate of sodium, when it may be dissolved in acetic acid. Phosphate and arsenite of lead, or other lead salts insoluble in acetic acid, may be dissolved in nitric acid, and estimated according to Dr. Schwarz's original method.

Assay of Galena in the Wet Way.

When in contact with metallic zinc, galena is readily decomposed by acids. Even oxalic, acetic, and dilute sulphuric acids are capable, when hot, of decomposing galena,—metallic lead being deposited and sulphuretted hydrogen gas set free,—while with hydrochloric acid the decomposition is peculiarly rapid and complete.

Galena is easily decomposed, also, even in the cold by dilute nitric acid in presence of zinc; but the reaction differs in this case from that just described—not metallic lead but free sulphur is deposited, while nitrate of lead goes into solution.

The reaction with zinc and hydrochloric acid has been employed with advantage by Mr. F. H. Storer, Professor of Chemistry in the Massachussetts Institute of Technology, for assaying galena, particularly the common American variety, which contains no other heavy metal besides lead. The details of the process are as follows:—Weigh out 2 or 3 grms. or more of the finely powdered galena. Place the powder in a tall beaker, together with a smooth lump of pure metallic zinc. Pour upon the mixed mineral and metal 100 or 150 c.c. of dilute hydrochloric acid which has been previously warmed to 40° or 50° C.; cover the beaker with a watch-glass or broad funnel, and put it in a moderately warm place.

Hydrochloric acid fit for the purpose may be prepared by diluting 1 volume of the ordinary commercial acid with 4 volumes of water. For the quantity of galena above indicated, the lumps of zinc should be about an inch in diameter by a quarter of an inch thick; they may be readily obtained by dropping melted zinc upon a smooth surface of wood or metal.

The zinc and acid should be allowed to act upon the mineral during fifteen or twenty minutes in order to ensure complete decomposition. Any particles of galena which may be thrown up against the cover or sides of

the beaker should, of course, be washed back into the liquid. It is well, moreover, to stir the mixture from time to time with a glass rod.

When all the galena has been decomposed, as may be determined by the facts that the liquid has become clear, and that no more sulphuretted hydrogen is evolved, decant the liquid from the beaker into a tolerably large filter of smooth paper, in which a small piece of metallic zinc has been placed. Wash the lead and zinc in the beaker as quickly as possible with hot water, by decantation, until the liquid from the filter ceases to give an acid reaction with litmus paper; then transfer the lead from the beaker to a weighed porcelain crucible. In order to remove any portions of lead which adhere to the lump of zinc, the latter may be rubbed gently with a glass rod, and afterwards with the finger or a piece of caoutchouc, if need be. Wash out the filter into an evaporating dish, remove the fragment of zinc, and add the particles of lead thus collected to the contents of the crucible. Finally, dry the lead at a moderate heat in a current of ordinary illuminating gas, and weigh.

The lead may be conveniently dried by placing the crucible which contains it in a small cylindrical air-bath of Rammelsberg's pattern, provided with inlet and outlet tubes of glass, reaching almost to the bottom of the bath.

When the process is conducted as above described, the lead undergoes no oxidation; hence there is no occasion for igniting the precipitate in a reducing gas. The precipitate needs only to be dried out of contact with the air.

If desirable, the sulphur in the galena could be determined at the same time as the lead, by arresting the sulphuretted hydrogen in the ordinary way.

If the mineral to be analysed is contaminated with a siliceous or other insoluble gangue, the metallic lead may be dissolved in dilute nitric acid after weighing, and the insoluble impurity collected and weighed by itself. In the case of galenas which contain silver, antimony, copper, or other metals, precipitable by zinc, the proportion of each metal must be determined by assay or analysis in the usual way after the total weight of the precipitated metals has been taken.

Besides galena, almost any of the ordinary lead compounds may evidently be assayed by the method above described. For example, metallic lead may be precipitated quickly and completely from the sulphate, chromate nitrate, oxide, and carbonate—and with peculiar ease from the chloride—by means of zinc and hydrochloric acid. The method would also furnish an easy qualitative test for the detection of baryta in white-lead. When applied to the analysis of nitrate of lead, it would probably be best to decompose the nitrate by means of a solution of chloride of sodium before adding the zinc and hydrochloric acid.

In all these cases the decomposition of the lead salt by the zinc is so complete that no trace of colouration is produced when sulphuretted hydrogen is added to the liquid decanted from the metallic lead.

Attempts to determine sulphur and lead in the same portion of galena, by means of the reaction of zinc and dilute nitric acid above described, give no satisfactory results. The free sulphur obtained by treating galena with zinc and ordinary nitric acid, diluted with 3, 4, and 5 volumes of water, always retains a small quantity of lead, while a certain amount of sulphuric acid is found in the clear liquid. It is, in short, well nigh, or quite, impossible to avoid the secondary reactions between zinc and nitrate of lead, and between sulphur and nitric acid, which set in as soon as, or just before, the last traces of the galena have been decomposed.

Detection of Peroxide of Lead in Litharge.

Heat the litharge in a test-tube with chloride of sodium and bisulphate of potassium, and introduce into the tube a slip of paper coloured with a solution of indigo. If any peroxide be present chlorine is disengaged, which bleaches the paper.

Separation of Lead from Copper.

Supposing the two metals to be present in a nearly neutral solution, acidulate with acetic acid and add a solution of bichromate of potassium. A yellow precipitate of chromate of lead falls down which is insoluble in acetic acid. If only a trace of lead be present the precipitation will not take place immediately. Should the original solution contain free mineral acid, an excess of acetate of sodium must be added instead of acetic acid. The precipitated chromate of lead for quantitative purposes is best converted into sulphate before weighing (see p. 211).

Separation of Lead from Mercury.

Rose's method of precipitating protochloride of mercury from the solution by the addition of hydrochloric acid and phosphorous acid, is not applicable to the separation of mercury and lead. A portion of the lead is precipitated in the state of chloride with the protochloride of mercury. A better plan for analysing a mixture of the salts of these two metals is to add sulphuric acid, and then alcohol forming about one-sixth of the volume of the liquid. If this does not contain sufficient hydrochloric acid, and if the proportion of sulphuric acid is insufficient, yellow subsulphate of mercury may be precipitated, which is avoided by the addition of sulphuric acid. The sulphate of lead requires washing with weak alcohol acidulated with sulphuric acid.

Separation of Lead from Silver.

This is, perhaps, the most appropriate place to describe the valuable improvements which Mr. D. Forbes has made in the separation of silver and lead before the blowpipe. This assay process is in all cases based upon the reduction to a metallic state of all the silver contained in the compound in question along with more or less metallic lead, which latter metal, when not already present in sufficient quantity in the substance itself under examination, is added in the state of granulated lead to the assay previous to its reduction. The globule of silver-lead thus obtained, if soft and free from such elements as would interfere with its treatment upon the cupel, may then be at once cupelled before the blowpipe until the pure silver alone remains upon the bone-ash surface of the cupel; but if not, it is previously submitted to a scorifying or oxidating treatment upon charcoal until all such substances are either slagged off or volatilised, and the resulting silver-lead globule cupelled as before.

As, therefore, the final operation in all silver assays is invariably that of cupelling the silver-lead alloy obtained from the previous reduction of the substance, effected by methods differing according to the nature of the argentiferous ore or compound under examination, it is here considered advisable to introduce the description of the silver assay by an explanation of this process.

In the ordinary process of cupellation in the muffle, bone-ash or other cupels are employed, of a size large enough to absorb the whole of the litharge produced from the oxidation of the lead in the assay.

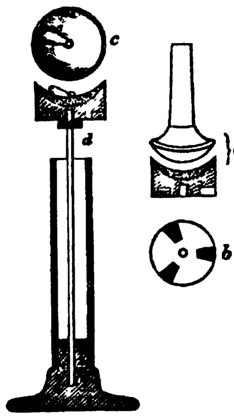
This, however, should not be the case when using the blowpipe; for as the heating powers of that instrument are limited, it is found in practice much better to accomplish this result by two distinct operations—the first being a concentration of the silver-lead, in which the greater part of the lead is converted by oxidation into litharge remaining upon, but not, or only very slightly, absorbed by the bone-ash cupel; and the second in cupelling the small concentrated metallic bead so obtained upon a fresh cupel until the remaining lead is totally absorbed by the cupel and the silver left behind in a pure state. By this means a much larger weight of the silver-lead alloy can be submitted to assay, and, for reasons hereafter to be explained, much much more exact results are obtained than would be the case when the cupellation is conducted at one operation in the ordinary manner.

The apparatus used by Mr. Forbes for these operations are shown to a scale of one-half their real size in the woodcuts (Fig. 6, *a* to *d*).

In Fig. 6, *a*, is represented in section a small cylindrical mould of iron, seven-tenths of an inch in diameter, and about four-tenths high, in which is turned a cup-shaped, nearly hemispherical depression, two-tenths of an inch deep in centre, the inner surface of which is left rough, or marked with

minute ridges and furrows for the purpose of enabling it to retain more firmly the bone-ash lining, which is stamped into it by means of the polished bolt also shown in the figure. This mould rests upon the stand, *d*, having for this purpose a small central socket in its base, into which the central pivot of the stand enters. The socket is seen in the ground plan, *b*, of the base of the mould, which shows likewise three small grooves or slots made in same to enable a steady hold to be taken of it, when hot, by the forceps. The stand itself is composed of a small turned ivory or wood base, fixed into a short piece of strong glass tubing, which, from its non-conducting powers, serves as an excellent handle. In centre of the base a slight iron rod rising above the level of the glass outer tube serves as a support for the cupel mould, into the socket in the base of which it enters.

FIG. 6.



Bone-ash is best prepared by burning bones which have been previously boiled several times, so as to extract all animal matter. The best bone-ash is made from the core-bone of the horns of cattle well boiled out and burned. The ash from this is more uniform than from the other bones, which have in general a very compact enamel-like exterior surface, whilst the interior is of a much softer nature.

Concentration of the Silver-Lead.—A cupel is prepared by filling the above-described cupel mould with bone-ash powder not finer than will pass through a sieve containing from forty to fifty holes in the linear inch ; it should be well dried and kept in an air-tight bottle, and, when used, the whole must be pressed down with the bolt, using a few taps of the hammer. It is then heated strongly in the oxidating blowpipe flame, in order to drive off any hygroscopic moisture. The bone-ash surface of the cupel, after heating, should be smooth, and present no cracks ; if the reverse, these may be removed by using the bolt again and re-heating.* The silver-lead, beaten on the anvil into the form of a cube, is placed gently upon the surface of the bone-ash, and, directing a pretty strong oxidating flame on to its surface, it is fused, and quickly attains a bright metallic appearance, and commences to oxidise with a rapid rotatory movement. (Occasionally, when the assay is large, and much copper or nickel present, the globule may, under this operation, cover itself with a crust of oxide of lead, or solidify ; in such cases direct the blue point of a strong flame steadily on

* These precautions are very important, as the slightest trace of moisture in the substance of the bone-ash would inevitably cause a spirting of the metal during the operation.

to one spot on the surface of the lead-globule until it commences oxidating and rotating. In some cases where much nickel is present, an infusible scale, impeding or even preventing this action, may form, but will disappear on adding more lead—say from 3 to 6 grains, according to the thickness of this scale or crust). When this occurs the cupel is slightly inclined from the lamp, a fine blue point is obtained by placing the blowpipe nozzle deeper into the lamp, and the flame is directed at about an angle of 30° on to the globule—not, however, so near as to touch it with the blue point, but only with the outer flame, so moderating it as to keep the assay at a gentle red heat, and not allowing the rotation to become too violent.

This oxidating fusion should be carried on at the lowest temperature sufficient to keep up the rotatory movement, and to prevent a crust of litharge accumulating upon the surface of the globule, but still sufficiently high to hinder the metallic globule from solidifying. Should this, however, happen, a stronger flame must be employed for a moment until the metal is again in rotation; such interruptions should, however, be avoided. The proper temperature can only be learned by practice, a too high temperature is still more injurious, causing the lead to volatilise, and, if rich in silver, carry some of that metal mechanically along with it. The litharge, also, instead of remaining on the cupel would be absorbed by the bone-ash, and as the surface of the metallic globule is covered by a too thin coating of fused litharge, some silver may be absorbed along with the litharge. In this operation, in order to avoid loss of silver, the fused globule should be always kept in contact with the melted litharge.

By the above treatment the air has free access to the assay, and the oxidation of the lead and associated foreign metals goes on rapidly. The surface of the melted globule, when poor in silver, shows a brilliant play of iridescent colours, which does not take place when very rich in silver. The litharge is driven to the edge of the globule, heaping itself up and solidifying behind and around it. When the globule becomes so hemmed in by the litharge as to present too small a surface for oxidation, the cupel is moved so as to be more horizontal (having been previously kept in an inclined position), thus causing the lead-globule to slide by its own weight on one side, and expose a fresh surface to the oxidising action. When the lead is pure, the litharge formed has a reddish-yellow colour, but, if copper is present, is nearly black.

In concentrating silver-lead, it must be remembered that an alloy of lead and silver, if in the proportion of about 86 per cent silver along with 14 per cent lead, when cooled slowly in the litharge behaves in a manner analogous to the spitting of pure silver, throwing out a whitish-grey pulverulent excrescence rich in silver. For this reason, therefore, the concen-

tration above described should be stopped when the globule is supposed to contain about six parts silver along with one part in weight of lead. In case, however, this limit should have been exceeded, it is advisable at once to push the concentration still further until the silver globule contains but very little lead. In practice, with poor ores, it is usual to concentrate the lead until the globule is reduced to the size of a small mustard seed, or in rich ores to some two or three times that size. Upon arriving at this point, the cupel is withdrawn very gradually from the flame, so that the cooling shall take place as slowly as possible until the globule has solidified in its envelope of litharge. If cooled too quickly, the litharge, contracting suddenly, would throw out the globule, or even cause it to spirt; in such case it should be touched by the point of the blue flame so as to fuse it to a round globule, which is cooled slowly as before described. The globule is now reserved for the next operation, for which purpose it is, when quite cold, extracted from the litharge surrounding it.

Cupellation.—The bone-ash required for this process should be of the best quality and in the most impalpable powder, prepared by elutriating finely-ground bone-ash, and drying the product before use.

The cupel still hot from the last operation is placed upon the anvil, and the crust of litharge, with its enclosed metallic bead, gently removed, leaving the hot coarse bone-ash beneath it in the mould; upon this a small quantity of the elutriated bone-ash is placed, so as to fill up the cavity, and the whole whilst hot stamped down by the bolt, previously slightly warmed, with a few taps of the hammer. The cupel thus formed is heated strongly in the oxidating flame, which should leave the surface perfectly smooth, and free from any fissures or scales; if such appear, the bolt must again be used, and the cupel re-heated. In this process it is very important that the cupel should possess as smooth a surface as possible, whilst at the same time the substance of the cupel beneath should not be too compact, so as thereby to permit the litharge to filter through and be readily absorbed, leaving the silver bead upon the smooth upper surface.

The bead of silver-lead obtained from the last operation is taken out of the litharge in which it is embedded, and, after removing any trace of adherent bone-ash or litharge, is slightly flattened to prevent its rolling about upon the surface of the cupel.

It is now put into the cupel prepared as before described, placing it on the side furthest from the lamp and a little above the centre of the cupel, which is now inclined slightly towards the lamp, and is heated by the oxidating flame directed downwards upon it, thus causing the globule when fused and oxidating to move of itself into the centre of the cupel. The

cupel is now brought into a horizontal position, and the flame, directed on to it at an angle of about forty-five degrees, is made to play upon the bone-ash surface immediately surrounding the globule, without, however, touching it; so as to keep this part of the cupel at a red heat sufficiently strong to insure the globule being in constant oxidising fusion, at the same time to cause the perfect absorption of the litharge, and to prevent any scales of litharge forming upon the surface of the cupel under the globule, which would impede the oxidation, as well as prevent the silver bead being easily detached at the conclusion of the operation. Should the heat at any time be too low and the globule solidify, it must be touched for an instant with the point of the flame and proceeded with as before. Should (in consequence of the bone-ash not having been sufficiently heated to absorb the litharge perfectly) a little litharge adhere pertinaciously to the globule, or a particle of the bone-ash cupel attach itself, the cupel should be slightly inclined, so as to allow the globule to move by its own weight on to another and clean part of the cupel, leaving the litharge or bone-ash behind it; but, if not sufficiently heavy to do so, a small piece of pure lead may be fused to it in order to increase its weight, and so allow of the same proceeding being adopted.

By slightly inclining the cupel stand, and moving it so as to present in turn all parts of the surface surrounding the globule to the action of the flame, the cupellation proceeds rapidly. If, however, the assay contains very little silver, it will be found necessary to move the globule from one spot to another on the cupel, in order to present a fresh surface for absorbing the litharge formed; this is done by simply inclining the cupel stand, remembering that the bone-ash surrounding the globule must always be kept at a red heat, without ever touching the globule itself by the flame.

In assays rich in silver a play of iridescent colours appears some seconds before the "brightening," which disappears the moment silver becomes pure; as soon as this is observed the cupel should be moved in a circular manner, so that the globule is nearly touched all round by the point of the blue flame, and this is continued until the surface of the melted silver is seen to be quite free from any litharge, upon which it is very gradually withdrawn from the flame so as to cool the assay by degrees very slowly, in order to prevent "spitting."

When the silver-lead is very poor, this play of colours is not apparent, and as soon as the rotatory movement of the globule ceases, the heat must be increased for an instant in order to remove the last thin but pertinacious film or scale of litharge, and subsequently the assay is cooled gradually; when cold it should, whilst still upon the cupel, be examined by a lens to see whether the bead possesses a pure silver colour, as if not it must be re-heated,

Frequently, when the "brightening" takes place, the silver globule is found to spread out, and, after cooling, although of a white colour, is found to appear somewhat less spherical or more flattened in shape than a corresponding globule of pure silver would be. This arises from the presence of copper still remaining in the silver, and in such cases a small piece of pure lead (about from half a grain to one and a half grains in weight, according to size of assay) should be fused on the cupel along with the silver, and the cupellation of the whole conducted as before on another part of the cupel, when the silver globule will be obtained pure and nearly spherical in shape. Sometimes the silver globule in "brightening" may still remain covered with a thin film of litharge, although otherwise pure; this arises from too little heat having been employed in the last stage of the operation, and consequently the bead should be re-heated in a strong oxidating flame until this litharge is absorbed, and the globule, after slow cooling, appears pure.

If the instructions here given be strictly attended to, it will be found, after some practice, that very accurate results may be obtained in the blowpipe assay for silver, and that no difficulty will be found in detecting the presence and determining the amount of silver present, even when in as small a quantity as half an ounce to the ton. When substances containing very little silver or less than that amount are examined, several assays should be made, and the silver-lead obtained concentrated separately, after which the various globules should be united and cupelled together in one operation.

It is hardly necessary to remark that the lead employed in assaying should be free from silver, or, if not, its actual contents in silver should be determined, and subtracted from the amount found in the assay.

Assay lead containing less than one-quarter of an ounce to the ton of lead can readily be obtained, or can be made by precipitating a solution of acetate of lead by metallic zinc, rejecting the first portion of lead thrown down. In all cases the lead should be fused and granulated finely—the granulated lead for use in these assays being previously passed through a sieve containing forty holes to the linear inch. It is also useful to have some lead in the form of wire, as being very convenient for adding in small portions to assays when on the cupel.

Determination of the Weight of the Silver Globule obtained on Cupellation.—As the amount of lead which can, by the method above described, be conveniently cupelled before the blowpipe is necessarily limited, the silver globule which remains upon the bone-ash surface of the cupel at the end of the operation is, when substances poor in silver have been examined, frequently so very minute that its weight could not be determinated with correctness by the most delicate balances in general use.

Globules of silver of far less weight than one-thousandth are distinctly

visible to the naked eye—a circumstance which induced Harkort to invent a volumetrical scale based upon the measurement of the diameters of the globules, which scale in practice has been found of very great utility in the blowpipe assay of silver.

The scale for this purpose consists of a small strip of highly polished ivory about 6¼ inches long, ⅜ inch broad, and ⅛ inch in thickness, on which are drawn, by an extremely fine point, two very fine and distinct lines emanating from the lower or zero point, and diverging upwards until, at the distance of exactly six English standard inches, they are precisely four-hundredth parts of an inch apart. This distance (six inches) is divided into 100 equal parts by cross lines numbered in accordance from zero upwards. It is now evident, if a small globule of silver be placed in the space between these two lines, using a magnifying glass to assist the eye in moving it up or down until the diameter of the globule is exactly contained within the lines themselves, that we have at once a means of estimating the diameter of the globule itself, and therefrom are enabled to calculate its weight.

As the silver globules which cool upon the surface of the bone-ash cupel are not true spheres, but are considerably flattened on the lower surface where they touch and rest upon the cupel, it follows that the weight of globules corresponding in diameter to the extent of divergence at the different degrees of the scale cannot be calculated directly from their diameters as spheres, but require to have their actual weight experimentally determined in the same manner as employed by Plattner.

The table here appended is an abstract of one calculated by Mr. Forbes, and in one column shows the diameter in English inches corresponding to each number or degree of the scale itself, and in the next column the respective weights of the flattened spheres which correspond to each degree or diameter. For ordinary purposes the intermediate weights may safely be obtained by interpolation, but if great accuracy is needed the full table should be consulted. It is given in the "Chemical News" for June 7th, 1867, vol. xv., p. 281.

These weights are calculated from the following data, found as the average result of several very careful and closely approximating assays, which showed that globules of silver exactly corresponding to No. 95 on this scale, or 0·038 inch in diameter, possessed a weight of 0·0475573 grs. From this the respective weights of all the other numbers or degrees on this scale were calculated, on the principle that solids were to one another in the ratio of the cubes of their diameters. This mode of calculation is not, however, absolutely correct in principle, for the amount of flattening of the under surface of the globule diminishes in reality with the decreasing volume of the globule. In actual practice, however, this difference may be

assumed to be so small that it may be neglected without injury to the correctness of the results.

The smaller the diameter of the globule, the less will be the difference or variation in weight in descending the degrees of this scale, since the globules themselves vary in weight with the cubes of their diameters; for this reason, also, all such globules as come within the scope of the balance employed should be weighed in preference to being measured, and this scale should be regarded as more specially applicable to the smaller globules beyond the reach of the balance.

No. on scale.	Greatest diameter in inches.	Weight of globule in grains.
1	0·0004	0·00000005
2	0·0008	0·00000044
3	0·0012	0·00000149
4	0·0016	0·00000355
5	0·0020	0·0000069
6	0·0024	0·0000119
7	0·0028	0·0000190
8	0·0032	0·0000284
9	0·0036	0·0000403
10	0·0040	0·0000554
15	0·0060	0·0001872
20	0·0080	0·0004437
25	0·0100	0·0008667
30	0·0120	0·0014976
40	0·0160	0·0035550
50	0·0200	0·0069335
60	0·0240	0·0119815
70	0·0280	0·0190256
80	0·0320	0·0284000
90	0·0360	0·0404368
100	0·0400	0·0554688

Cupellation Loss.—This term is applied to indicate a minute loss of silver, unavoidably sustained in the process of cupellation, which arises from a small portion of that metal being mechanically carried along with the litharge into the body of the cupel. The amount of this loss increases with the quantity of lead present in the assay (whether contained originally in the assay or added subsequently for the purpose of slagging off the copper, &c.); it is relatively greater as the silver globule is larger, but represents a larger percentage of the silver actually contained in the assay in proportion as the silver globule obtained diminishes in size. It has, however, been experimentally proved that in assays of like richness in silver, this loss remains constant when the same temperature has been employed and similar weights of lead have been oxidised in the operation.

In the blowpipe assay this loss is not confined to the ultimate operation of cupellation, but occurs, though in a less degree, in the concentration of

the silver-lead, and in the previous scorification of the assay, had such operation preceded the concentration. The total loss in the blowpipe assay is found, however, to be less than in the ordinary muffle assay, since, in the latter case, the whole of the oxidised lead is directly absorbed by the cupel.

In mercantile assays of ore it is not customary to pay attention to the cupellation loss, and the results are usually stated in the weight of silver actually obtained. Where, however, great accuracy is required, especially when the substances are very rich in silver, the cupellation loss is added to the weight of the silver globule obtained in order to arrive at the true percentage.

The amount to be added for this purpose is shown in the annexed table, which is slightly modified from Plattner's:—

Actual percentage of silver found by assay.	Cupellation loss, or percentage of silver to be added to the actul percentage found by assay in order to show the true percentage of silver contained in same. The entire amount of lead in or added to the assay being the following multiples of the original weight of assay:—									
	1	2	3	4	5	6	8	11	13	16
99·75 } 99·50 }	0·25	0·32	0·39	0·45	0·50	—	—	—	—	—
90 ..	0·22	0·29	0·36	0·42	0·47	0·69	0·83	—	—	—
80 ..	0·20	0·26	0·33	0·39	0·44	0·64	0·75	—	—	—
70 ..	0·18	0·23	0·29	0·35	0·40	0·58	0·68	0·82	—	—
60 ..	0·16	0·20	0·26	0·30	0·36	0·52	0·61	0·74	—	—
50 ..	0·14	0·17	0·23	0·26	0·32	0·46	0·54	0·65	—	—
40 ..	0·12	0·15	0·20	0·22	0·27	0·39	0·46	0·55	0·62	—
35 ..	0·11	0·13	0·18	0·18	0·25	0·36	0·42	0·50	0·57	—
30 ..	0·10	0·12	0·16	0·16	0·22	0·32	0·38	0·45	0·51	—
25 ..	0·09	0·10	0·14	0·14	0·20	0·29	0·34	0·40	0·45	—
20 ..	0·08	0·09	0·12	0·12	0·17	0·25	0·29	0·35	0·39	0·45
15 ..	0·07	0·08	0·10	0·11	0·15	0·20	0·23	0·28	0·32	0·37
12 ..	0·06	0·07	0·09	0·10	0·13	0·17	0·19	0·23	0·26	0·32
10 ..	0·05	0·06	0·08	0·09	0·11	0·15	0·17	0·20	0·23	0·27
9 ..	0·04	0·05	0·07	0·08	0·10	0·14	0·16	0·18	0·21	0·25
8 ..	0·03	0·04	0·06	0·07	0·09	0·13	0·15	0·16	0·18	0·22
7 ..	0·02	0·03	0·05	0·06	0·08	0·12	0·13	0·14	0·16	0·20
6 ..	0·01	0·02	0·04	0·05	0·07	0·10	0·11	0·12	0·14	0·17
5 ..	—	0·01	0·03	0·04	0·06	0·09	0·10	0·11	0·12	0·14
4 ..	—	—	0·02	0·03	0·05	0·07	0·08	0·09	0·10	0·11
3 ..	—	—	0·01	0·02	0·04	0·05	0·06	0·07	0·08	0·09
2 ..	—	—	—	0·01	0·03	0·04	0·04	0·05	0·06	0·07
1 ..	—	—	—	—	0·01	0·03	0·03	0·04	0·04	0·05

The use of the above table is best explained by an example, as the following:—An assay to which there had been added, in all, five times its weight of assay lead, gave a globule of silver equivalent to 6 per cent. Upon referring to the table, it will be seen that the cupellation loss for this would be 0·07; consequently, the true percentage of silver contained in the

assay would be 6·07. This table is only extended to whole numbers, but fractional parts can easily be calculated from the same.

When the globules of silver are so minute that they cannot be weighed, but must be measured upon the scale, the cupellation loss should not be added, since, as a rule, it would be less than the difference which might arise from errors of observation likely to occur when measuring their diameters upon the scale.

In the case of beginners, it will be found that the cupellation is usually carried on at too high a temperature, and that thereby a greater loss is occasioned than would be accounted for by the above table. After some trials, the necessary experience will be acquired in keeping up the proper temperature at which this operation should be effected.

It is not necessary to consider in detail the processes requisite for extracting the silver contents (in combination with lead) from the various silver ores and other argentiferous compounds which are met with in nature or produced in the arts, as this would be to exceed the limits of analysis proper. The following classification of substances will, however, be found convenient:—

I. Metallic Alloys.

A. Capable of direct cupellation.

a. Consisting chiefly of lead or bismuth: silver, lead, and argentiferous bismuth, native bismuthic silver.

b. Consisting chiefly of silver: native silver, bar silver, test silver, precipitated silver, retorted silver amalgam, standard silver, alloys of silver with gold and copper.

c. Consisting chiefly of copper: native copper, copper ingot, sheet or wire, cement copper, copper coins, copper-nickel alloys.

B. Incapable of direct cupellation.

a. Containing much copper or nickel, with more or less sulphur, arsenic, zinc, &c.: unrefined or black copper, brass, german silver.

b. Containing tin: argentiferous tin, bronze, bell metal, gun metal, bronze coinage.

c. Containing antimony, tellurium, or zinc.

d. Containing mercury: amalgams.

e. Containing much iron: argentiferous steel, bears from smelting furnaces.

II. Mineralised Compounds.

a. Silver and other ores, furnace products, sweeps, and products of the arts containing sulphides, arsenides, and other compounds of the metals in combination with more or less earthy matter.

b. Argentiferous sulphide of molybdenum.

c. Substances nearly free from sulphides or arsenides, but containing chlorine, iodine, or bromine.

d. Argentiferous litharge and other easily reducible oxides.

To give information on the treatment of these substances belongs to the subject of assaying, a branch of analysis of which we have not space now to treat. The reader who wishes to follow out the subject is referred to "A Manual of Practical Assaying,"* edited by the author of this work.

Separation of Lead from Zinc.

The best method of separating small quantities of lead from zinc, as in the analysis of commercial spelter, is to add bichromate of potassium and acetic acid to the neutral solution of the metals. A trace of lead causes the formation of a yellow precipitate. For further particulars see p. 211.

Separation of Lead from Barium, when in the form of Sulphates.

Hyposulphite of sodium dissolves sulphate of lead, and may be used to separate this salt from the sulphate of barium. To effect this separation a concentrated solution of the hyposulphite must be added to the mixture of the two salts, and the whole gently warmed, taking care that the temperature does not exceed 68° C.; at a higher temperature sulphite of lead is formed, which is insoluble in the hyposulphite.

The residue of sulphate of barium is carefully washed and weighed; to control the results the lead in the hyposulphite may be estimated.

THALLIUM.

Detection of Thallium in Minerals.

The optical process of detecting thallium in a mineral is very simple. A few grains of the ore are crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen's gas-burner, and examining the light by means of a spectroscope, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opaque screen in the eye-piece of spectroscope to protect the eye from the glare of the sodium line, thallium may be detected in half a grain of mineral, when it is present only in the proportion of 1 to 500,000. The sensitiveness of this spectrum reaction is so great that no estimate can be arrived at respecting the probable amount of thallium present. Before deciding whether a deposit or mineral contains sufficient of the metal to be worth extracting, it is necessary to make a rough analysis in the wet way by methods which will be subsequently described.

* London: Longmans and Co., 1868.

The best method of separating silver and thallium, when together as chlorides or iodides, consists in reducing the metals by the addition of a rod of pure zinc to the mixture. When the reaction is complete, remove the zinc, and wash with hot water till the washing waters are free from chlorine. Then heat with dilute sulphuric acid, which dissolves the thallium and leaves the silver, or dissolve the whole in nitric acid and precipitate the silver with sulphuretted hydrogen.

Separation of Thallium from Nickel, Cobalt, or Manganese.

Add sulphite of sodium in excess to the solution, so as to be certain that all the thallium is in the state of protosalt, then add excess of carbonate of sodium and boil. The thallium will remain in solution, whilst the other metals will be precipitated. Filter off and add iodide of potassium to the filtrate; this will precipitate insoluble iodide of thallium in the form of a yellow powder. When the thallium is present in traces only, it is better to add iodide of potassium direct to the liquid, without separating the other metals with carbonate of sodium.

Separation of Thallium from Iron.

Certain kinds of iron pyrites constitute the richest natural source of thallium. At page 228 the methods of separating thallium from thalliferous pyrites on the large scale are fully described. Thallium may be readily detected in thalliferous pyrites in the following manner:—Dissolve the finely powdered mineral in nitro-hydrochloric acid; evaporate with excess of sulphuric acid until the nitric acid is evolved; dissolve in water; and add sulphite of sodium to reduce the iron and thallium to the state of proto-salts. On adding iodide of potassium, and allowing the liquid to stand for some time, a bright yellow precipitate of iodide of thallium will separate. This test is sufficiently delicate to show thallium in a few grains of a pyrites which does not contain more than one part in 10,000.

If the iron only is in the state of peroxide (as in the case of thallium-iron alum) the separation may be effected by ammonia, which precipitates the sesquioxide of iron, and leaves the thallium in solution.

Separation of Thallium from Zinc.

Thallium is present in many specimens of blende and calamine, especially from Nouvelle Montagne and the neighbourhood of Spa, in Belgium. In such cases it accompanies the zinc in most of its preparations, and may, therefore, be frequently detected in the commercial metal. By proceeding in the following manner, the black residue which is left behind when zinc is dissolved in sulphuric acid will generally be found to contain thallium. Dissolve the residue in nitric acid; evaporate the solution with excess of

sulphuric acid; dissolve the residue in a small quantity of water; filter the liquid from sulphate of lead and add sulphite of sodium. Upon adding iodide of potassium to the solution the thallium will be precipitated.

When thallium is present in larger quantities precipitate the zinc with carbonate of sodium, which has no action on thallium.

Separation of Thallium from Chromium.

The chromates of thallium are insoluble in water, but readily soluble in hydrochloric acid, chlorine being evolved, and a soluble perchloride being produced. When boiled with hydrochloric acid and alcohol, these chromates are quickly decomposed, protochloride of thallium being precipitated, whilst sesquichloride of chromium remains in solution. Filter off and wash with alcohol, in which protochloride of thallium is insoluble.

INDIUM.

Preparation of Indium from Commercial Zinc.

Zinc from the Freiburg mines contains, besides a small quantity of lead, iron, arsenic, and cadmium, 0·0448 per cent of indium. To separate the indium the zinc is dissolved in dilute sulphuric or hydrochloric acid, and boiled until the evolution of gas ceases. The metallic precipitate left, when the precaution is taken to leave a little zinc undissolved, contains all the indium, together with the lead, &c. In the case of a solution containing indium—such as chloride of zinc,—the separation may be effected by means of acetate of sodium, indium having the property, like iron, of forming an insoluble basic salt. A little dilute sulphuric acid is first added to the solution containing indium, and carbonate of sodium is next added until, after stirring, a slight cloudiness remains; acetate of sodium is then added, and the mixture is boiled. In this way a basic sulphate of indium, containing a little iron and zinc, is precipitated. It is best to wash the precipitate by decantation, as the gelatinous precipitate rapidly clogs up the pores of filtering paper.

From a hydrochloric or nitric solution of indium the separation may be effected by carbonate of barium, which perfectly precipitates the oxide in the cold. The precipitate usually contains some iron, but no zinc.

Preparation of Indium from Blende.

Roast the indiferous blende and boil in dilute sulphuric acid; filter, nearly neutralise with carbonate of sodium, and then put clean plates of zinc into the solution. Scrape the reduced metals from time to time from the zinc, and preserve the precipitates separately. The purification of the indium is then easier in consequence of this fractional precipitation.

Purification of Indium.

To obtain the indium pure, the precipitate containing it is dissolved in nitric acid. Most of the lead is first removed by means of sulphuric acid; sulphuretted hydrogen is then passed through the liquor until the remainder of the lead, with the arsenic, cadmium, &c., are precipitated. The excess of sulphuretted hydrogen is then got rid of by boiling, and the liquor is next oxidised by means of chlorate of potassium, and precipitated by excess of ammonia. In this way a good deal of the zinc present passes into solution; a small quantity, however, remains with the precipitated oxides of iron and indium. The precipitate is now dissolved in dilute acetic acid, and again precipitated by sulphuretted hydrogen. A little zinc and iron still go down with the indium, and will after six precipitations; so for the perfect purification an additional operation is necessary. The mixed sulphides are dissolved in hydrochloric acid; in this solution the ferric chloride is reduced to ferrous chloride by the evolution of sulphuretted hydrogen. Carbonate of barium is now added, and then after twelve or twenty-four hours all the indium is found in the precipitate, free from all impurities but barium.

To obtain the metal, the oxide is carefully heated in a stream of hydrogen. In consequence of the volatility, the heat at first must not be great, and the stream of gas must be passed slowly. After the reduction the metal will be found in small silver-looking buttons, which can be fused together under cyanide of potassium.

BISMUTH.

Purification of Bismuth.

The best plan to purify bismuth is based on the fact that when a large quantity of water is added to its solution mixed with hydrochloric acid a completely insoluble precipitate of oxychloride of bismuth is obtained. Dissolve the metal in nitric acid and evaporate down with excess of hydrochloric acid; the residue consists of chloride of bismuth. Add concentrated hydrochloric acid and heat till the residue is dissolved; filter if necessary through a sand filter. Now pour the solution in a thin stream, with constant stirring, into a large quantity of cold distilled water. A white precipitate of oxychloride is produced, which may either be weighed as such or reduced to the metallic state by fusion with cyanide of potassium.

Detection of Phosphate of Calcium in Subnitrate of Bismuth.

Phosphate of calcium is sometimes met with in subnitrate of bismuth as an adulterant. It may be easily detected in the following way:—

To one part of the salt of bismuth dissolved in weak nitric acid add two parts of citric acid; dissolve with the aid of a little water; add an excess of solution of ammonia, and boil. Any phosphate present will be thrown down with continuous boiling of the solution.

Separation of Bismuth from Thallium.

These elements frequently occur together in minerals containing bismuth, and thallium may frequently be detected in medicinal preparations of bismuth, especially the carbonate. The bismuth compound is to be first obtained in the form of a dilute solution, any convenient acid being used for this purpose. A slight excess of carbonate of sodium is now added, and then a little cyanide of potassium free from sulphide. The mixture is to be gently warmed, and allowed to stand for ten minutes, then filtered, and a few drops of sulphide of ammonium added to the clear liquid. If the slightest trace of thallium were originally present in the bismuth compound, it will now be precipitated as a sulphide, which, upon gently heating the liquid (not to the boiling-point), gradually collects together in deep brown, almost black flakes, after the characteristic manner of sulphide of thallium.

This process is one of extreme delicacy; by means of it one part of thallium can be detected in the presence of more than 100,000 parts of bismuth. In some cases, the thallium is present in so small a quantity as to occasion only a slight darkening of the liquid when the sulphide of ammonium is added. Upon allowing this to digest at a gentle heat, it will generally collect in the form of a few flakes at the bottom. These may be collected together on a small filter, washed to the apex, and tested in the spectroscope. When the precipitate is only present in sufficient quantity to produce a faint dark stain on the filter-paper, the latter may be partially dried by pressure between blotting-paper, opened, and the stained surface scraped up with a knife. The dark fibres are now to be twisted up in a platinum wire loop, and held in the flame of the spectroscope, when they will give abundant indications of the presence of thallium.

Separation of Bismuth from Lead.

Add to the concentrated solution just enough hydrochloric acid to precipitate all the chloride of lead, but so that a few drops of water do not render the liquid turbid. Then add dilute sulphuric acid, the slow action of which is hastened by occasional agitation; finally, after having added alcohol and well mixed the whole by renewed agitation, allow the sulphate of lead to deposit. This precipitate is to be filtered and washed, first with alcohol containing a few drops of hydrochloric acid, and then with pure alcohol. The bismuth may be precipitated in the filtrate by dilution with a large quantity of water.

Determination of Bismuth in Lead Alloys.—The alloys are dissolved in nitric acid, the solution diluted with water, and the bismuth precipitated by a strip of pure lead. The precipitated bismuth, black in colour and in the state of powder, is quickly washed off the lead, and the solution of lead decanted; the bismuth is then washed, first with water and then with alcohol, filtered on a weighed filter, dried, and weighed.

Separation of Bismuth from Mercury.

To the solution containing the bismuth and mercury (as per-salt) add a large excess of hydrochloric acid to prevent the precipitation of oxychloride of bismuth, and then add phosphorous acid. On standing, the mercury will be precipitated in the form of protochloride. After the separation of the mercury add a large quantity of water, which precipitates the bismuth as oxychloride. Reduce this to the metallic state by fusion with cyanide of potassium.

CHAPTER IX.

ANTIMONY, TIN, ARSENIC, TELLURIUM, SELENIUM.

ANTIMONY.

Estimation of Antimony.

WHEN antimony is precipitated in the form of sulphide, instead of weighing it as such, Professor Wöhler advises that it be converted into antimoniate of oxide of antimony, (Sb_2O_3,Sb_2O_5), by complete oxidation with fuming nitric acid in a weighed porcelain crucible. To avoid ignition, the substance must be moistened with a few drops of dilute acid before adding the fuming acid. A prolonged digestion effects the complete solution of the pulverulent precipitate of sulphur. The excess of acid is then evaporated off carefully, and the residue calcined.

Mr. Sharples employs the following process in the precipitation of antimonous sulphide:—Into the solution, containing, as usual, tartaric and free hydrochloric acid, a current of sulphuretted hydrogen is to be passed, the liquid being, during the passage of the gas, gradually heated to the boiling-point. The boiling is then to be continued for fifteen or twenty minutes, the current of gas passing uninterruptedly until the voluminous sulphide has become a dense granular powder occupying but a small portion of the original volume of the sulphide. The sulphide may then be washed with great facility, and dried upon a sand filter at 200°—300° C. All the determinations of antimony made in the laboratory of the Lawrence Scientific School for some years have been executed in this manner, the results leaving nothing to be desired. Arsenious sulphide does not become granular and dense under the same circumstances.

Detection of Antimony in Sublimates.

In the examination of mineral bodies for antimony, the test substance is often roasted in an open tube for the production of a white sublimate. Dr. E. Chapman, Professor of Mineralogy at Toronto, recommends for the detection of antimony in this substance the following process—a method more especially available when the operator has only a portable blowpipe-case at his command:—The portion of the tube to which the chief part of

the sublimate is attached is to be cut off by a triangular file, and dropped into a test-tube containing some tartaric acid dissolved in water. This being warmed or gently boiled, a part at least of the sublimate will be dissolved. Some bisulphate of potassium—either alone, or mixed with some carbonate of sodium and a little borax, the latter to prevent absorption—is then to be fused on charcoal in a reducing flame; and the alkaline sulphide thus produced is to be removed by the point of the knife-blade, and placed in a small porcelain capsule. The hepatic mass is most easily separated from the charcoal by removing it before it has time to solidify. Some of the tartaric acid solution is then to be dropped upon it, when the well-known orange-coloured precipitate of sulphide of antimony will at once result.

In performing this test, it is as well to employ a somewhat large fragment of the test substance, so as to obtain a thick deposit in the tube. It is advisable also to hold the tube in not too inclined a position, in order to let but a moderate current of air pass through it; and care must be taken not to expose the sublimate to the action of the flame, otherwise it might be converted almost wholly into a compound of antimonious and antimonic acids, the greater part of which would remain undissolved in the tartaric acid. A sublimate of arsenious acid, treated in this manner, would, of course, yield a yellow precipitate, easily distinguishable by its colour, however, from the deep orange antimonial sulphide. The crystalline character, &c., of this sublimate would also effectually prevent any chance of misconception.

Separation of Antimony from Mercury.

These metals can readily be separated by precipitating the mercury as protochloride by hydrochloric acid and phosphorous acid, according to the plan previously described. The antimony being retained in solution with tartaric acid, which does not prevent the precipitation of the protochloride of mercury.

TIN.

Estimation of Protoxide of Tin.

Protoxide of tin dissolved in potash possesses the property of reducing cupro-potassic tartrate in the same way as glucose. The sensibility of this reagent is very great, as minute traces of protoxide of tin suffice to determine a deposit of protoxide of copper.

The solution containing protoxide of tin is treated with a slight excess of potash, so as to re-dissolve the precipitate first formed; cupro-potassic tartrate is added to the alkaline solution, and the whole boiled; a precipitate of protoxide of copper instantly forms. When only traces of oxide of tin exist in the liquid, the precipitate may not be apparent in the first few

moments, but it collects, and becomes perfectly visible after standing ten or twelve hours. During this reaction, the protoxide of tin passes to the state of stannic acid, and no longer reacts on the cupro-potassic reagent.

One equivalent of protoxide of tin reacting on two equivalents of binoxide of copper precipitates one equivalent of protoxide of copper.

In other words, 1·000 in weight of protoxide of copper obtained by the reduction of cupro-potassic tartrate, corresponds to 0·937 of protoxide of tin, or 0·825 of metallic tin. Arsenious acid, dissolved in potash, also reduces the cupro-potassic reagent, changing, meanwhile, to arsenic acid. Reduction does not take place so rapidly as with protoxide of tin; it is however, complete. One equivalent of arsenious acid, while changing to arsenic acid, reacts on four equivalents of binoxide of copper, precipitating two equivalents of protoxide of copper, $AsO_3+4(CuO)=AsO_5+2(Cu_2O)$.

1·000 of protoxide of copper, obtained by reducing the cupro-potassic reagent, corresponds to 0·692 of arsenious acid, or 0·524 of metallic arsenic.

No other metallic oxide soluble in potash exercises any action on the cupro-potassic reagent.

Estimation of Binoxide of Tin.

Tin when in the state of bichloride may be estimated volumetrically by precipitation with a standard solution of ferrocyanide of potassium; the operation is carried out in a similar way to the estimation of lead by ferrocyanide of potassium (see p. 211).

Assay of Tin Ores.

1. Mr. J. W. B. Hallett has found that tin-stone is very easily resolved by fusion with three or four times its weight of fluohydrate of potassium. The mineral must be finely pulverised. The fused mass is treated directly in the crucible with sulphuric acid to expel fluorine, after which, by adding water, filtering, and boiling the filtrate, the whole of the tin is thrown down as stannic acid, which is to be separated from traces of iron in the usual manner. This method of resolving the ore of tin is much more convenient than fusion with caustic alkalies, or with sulphur and carbonate of sodium.

2. M. Moissenet precipitates the metal from a solution of the chloride by means of zinc, and then melts the precipitated metal in stearic acid. His process comprises five operations:—

1. Purification of the ore by treatment with aqua regia.
2. Reduction of the residue in the presence of charcoal.
3. Solution of the tin and iron in hydrochloric acid.
4. Precipitation of the tin by means of zinc.
5. Fusion of the precipitate into a button in stearic acid.

The precipitation of tin by zinc is very rapid, and takes place in strongly acid solutions; but the amount of acid and the dilution of the chloride influence the condition of the precipitate. In some solutions it appears in brilliant needles, but in very dilute solutions, and always towards the end of an operation, it is only a muddy deposit. The author recommends that a button of zinc be suspended in the liquid by means of a copper wire. When the precipitation is finished the metal is collected and pressed into a porcelain capsule. The lump so formed is melted in a few minutes if a piece of stearine is added to it.

3. Referring to the well-known difficulty of obtaining all the tin in one button in a dry assay by the ordinary process, and the error of 5 or 10 per cent which may arise, M. C. Winkler suggests the addition of copper for the purpose of collecting together the tin.

The ore is finely pulverised and roasted, first by itself and then once or twice with charcoal or coke, to remove sulphur, arsenic, and antimony. The residue is then digested for a quarter or half an hour with hot hydrochloric acid, and afterwards well washed with hot water. Iron, manganese, and copper are more completely removed by fusion with bisulphate of potassium, and then treating with hydrochloric acid, and washing with water. Tungstic acid, if present, will now be removed by digesting with caustic potash or ammonia.

The oxide of tin, silica, &c., remaining are now mixed in a crucible with an equal weight of oxide of copper, and two or three parts of a flux, consisting of two parts anhydrous carbonate of sodium, one part white flour, and a quarter part borax glass. The whole is covered with a layer of common salt, upon which a piece of charcoal is laid. The crucible is heated first to a red and then to a dull white heat for an hour, after which a button containing the whole of the tin and copper reduced will be found at the bottom.

As pure oxide of copper may not be obtainable, a portion of every sample should be separately assayed. The weight of the tin will be found by subtracting the weight of the copper from that of the button.

4. The most uniformly successful process for the assay of tin ores has been found by the author to be the following:—The sample having been carefully selected, is first crushed by the hammer in a steel mortar, and then further reduced to powder in an agate mortar. 100 grains is a convenient quantity to be taken for analysis, and it is always advisable to make two independent experiments upon the same sample of ore, with the view of having a control; the highest result obtained is that upon which to place reliance, since the error must always be on the side of loss rather than excess. A couple of small Hessian crucibles, of about 3 ozs. capacity, are prepared in the first instance by ramming into the bottom of them a

small charge of powdered cyanide of potassium sufficient to form a layer of about half an inch in depth; the weighed quantities of tin ore are then intimately mixed with from four to five times their weight of the powdered cyanide, and the mortar rinsed with a small quantity of the pure flux, which is laid upon the top of the mixture. The crucibles are then heated in a moderate fire, or over a gas-blowpipe, and kept for the space of ten minutes at a steady fusion; they are then removed, gently tapped to facilitate the formation of a single button, and allowed to cool. Upon breaking the crucibles the reduced metal should present an almost silvery lustre, with a clean upper-layer of melted flux. The precaution should be taken of dissolving the latter in water for the purpose of being satisfied of the absence of any trace of reduced metal or heavy particles of the original ore. There is always contained in the commercial cyanide a sufficient quantity of alkaline carbonate to secure the perfect fusion of the siliceous gangue and other like impurities in the tin ore, but the operator should assure himself of the absence of copper and lead in the ore, either by preliminary treatment with hydrochloric acid, in which tin-stone is absolutely insoluble, or by testing the button of reduced tin, after hammering or rolling, for such metallic admixture. A minute trace of iron has been found in the melted buttons, and sometimes gold, but not so much as to add appreciably to their weight.

This process will sometimes furnish identical results, and when worked with ordinary care it may always be relied upon as giving numbers true to within ¼ per cent.

Separation of Tin from Antimony.

Mr. F. Wigglesworth Clarke has found that both sulphides of tin, if moist and freshly precipitated, are readily decomposed by moderately-long boiling with an excess of oxalic acid, sulphuretted hydrogen being given off. The monosulphide is converted into the insoluble, crystalline stannous oxalate, while the yellow disulphide is completely dissolved. The commercial "Mosaic gold," however, seems to be unacted upon by the reagent. In presence of an excess of oxalic acid, tin cannot be precipitated by sulphuretted hydrogen.

The sulphide of antimony behaves in a somewhat different manner. Although, upon long boiling with oxalic acid, considerable quantities of the metal are taken into solution, yet every trace of it may be re-precipitated by sulphuretted hydrogen.

By taking advantage of the solubility of the sulphides of tin in oxalic acid, this metal may be separated almost perfectly from antimony. To the solution containing the metals (this solution being prepared in the usual manner for the precipitation of the sulphides) add oxalic acid, in the

proportion of about 20 grms. of the reagent for every gramme of tin, taking care to have the whole so concentrated that the acid will crystallise out in the cold. Then heat to boiling, and pass in sulphuretted hydrogen for about twenty minutes. No precipitate appears at first; but, as soon as the liquid is saturated with the gas, the sulphide of antimony begins to fall, and, in a very few moments, is completely thrown down. Then, as usual, the whole should be allowed to stand about half-an-hour in a warm place, before filtering. Every trace of antimony is precipitated, so that in the filtrate from the sulphide nothing can be discovered by Marsh's test, nor can any antimony-stain be produced with zinc upon platinum.

The antimony always carries down a minute trace of tin with it; this trace, however, if the operation has been carefully performed, can scarcely be detected, and generally may be ignored with safety. If, however, the greatest accuracy is desired, it may be well to re-dissolve the sulphide of antimony in an alkaline sulphide, decompose the solution with an excess of oxalic acid, boil with a little strong sulphuretted hydrogen water, filter, and add the filtrate to the tin solution previously obtained.

Since the presence of oxalic acid interferes somewhat with the complete precipitation of tin by ordinary methods, some precautions are needed in the estimation of that metal after the separation. It can be thrown down as follows:—The solution, after being rendered slightly alkaline with ammonia, is mixed with enough sulphide of ammonium to re-dissolve the precipitate at first formed; an excess of acetic acid is added, and the whole allowed to rest several hours in a warm place. Acetic acid must be used, for stronger acids would be liable to set free some of the oxalic acid to re-dissolve the tin. The precipitate, which at first varies from white to pale yellow, rapidly darkens in colour, and seemingly consists of a mixture of oxide and sulphide of tin. It should be washed with a solution of nitrate of ammonium, and, after ignition, is weighed as binoxide of tin.

Mr. Clarke has also made a few experiments upon indirectly determining the proportions of tin and antimony in alloys of the two metals. He oxidises a weighed quantity of the alloy with nitric acid in a porcelain crucible, heats the resulting oxides with nitrate of ammonium, and then (regarding the tin as converted into binoxide, and the antimony into antimonic acid) calculates the proportions of the metals from the increase in weight. This method, although by no means giving accurate results, serves very well for rough approximate determinations. It is here cited simply as an easy and convenient process for obtaining a close idea of the constitution of any alloy composed of the two metals. Possibly the method might be so modified as to give accurate determinations.

The following process of separating tin from antimony has given very

accurate results :—Thoroughly oxidise the metallic alloy by means of strong nitric acid, evaporate the mass to dryness and gently heat it. Then fuse it in a silver dish with a large excess of caustic soda. After cooling dissolve in a minimum quantity of water, and then add one-third of its volume of strong alcohol. This precipitates antimoniate of sodium, whilst stannate of sodium remains in solution. Filter and wash, first with dilute, then with strong alcohol. Next dry the precipitated antimoniate of sodium and fuse it in a porcelain crucible, with an excess of cyanide of potassium. The antimony is reduced, and collects in a metallic button at the bottom of the crucible. The solution containing stannate of sodium is boiled to expel alcohol, diluted, acidulated with dilute sulphuric acid, and saturated with sulphuretted hydrogen gas. The precipitated sulphide of tin is then oxidised to binoxide of tin, and this then reduced to the metallic state by fusion with cyanide of potassium, as described on p. 249.

Separation of Tin from Bismuth.

To the strong hydrochloric solution of the two metals add a large excess of water. This produces an insoluble precipitate of oxychloride of bismuth, which may either be dried, and weighed in that state, or fused to a metallic button under cyanide of potassium. The tin will remain in solution.

Separation of Tin from Thallium.

When these two metals occur together in a liquid, they may be separated by adding an excess of sulphide of ammonium to the alkaline solution. Sulphide of thallium will be precipitated, whilst the tin will remain in solution.

Sulphuretted hydrogen passed through an acid solution containing tin and thallium, precipitates the tin, but a little thallium is carried down by the sulphide of tin.

Separation of Tin from Lead.

To detect and separate small quantities of lead in the presence of a great excess of tin, treat a small quantity of the metal with an excess of nitric acid, diluted with three times its weight of water, boil the mixture, filter, and then drop into the solution a crystal of iodide of potassium. If only one ten-thousandth part of lead is present, a yellow precipitate is formed, which does not disappear on adding an excess of ammonia.

Separation of Tin from Copper (Analysis of Gun and Bell Metal, containing, besides, traces of Lead, Zinc, and Iron).

The following process has been employed for some years in H. Sainte-Claire Deville's laboratory at the Ecole Normale :—Dissolve about 5 grms.

of the alloy in strong nitric acid contained in a flask provided with a funnel in the neck to prevent loss by spirting. When quite dissolved boil the strong solution for about twenty minutes; dilute with two or three times its bulk of water and boil again for the same time. Separate the insoluble oxide of tin by decantation, or filtration, and weigh after calcining it. (The oxide of tin is sometimes rose-coloured, owing to the presence of minute traces of gold; this may be disregarded.) The nitric acid solution freed from the tin is evaporated on a small platinum or porcelain dish, and the residue is calcined at a dull red heat. In this manner a mixture of oxides is obtained in sufficient quantity to suffice for at least two analyses.

About 2 grms. of the finely pulverised oxides are placed in a small platinum or porcelain boat, and thence introduced into a small glass tube closed with a good cork suitable for weighing. The boat, the tube, and the cork having been previously weighed, the weight of the oxides is obtained after they have been heated to dull redness in the apparatus, through which a current of dry air circulates. After having weighed the whole the current of air is replaced by dry hydrogen, and the tube is heated over a lamp until the contents cease to lose weight. It then contains unreduced oxide of zinc, together with copper, lead, and iron in the metallic state; the colour of the product shows the operator when the experiment is concluded. On weighing again the loss of weight indicates with great accuracy the amount of oxygen contained in the oxides of these three metals.

If the iron and lead are present in inappreciable quantities, by multiplying this loss by 5 will be given very nearly the weight of copper present, and, in consequence, the composition of the alloy itself. In an approximate analysis of gun-metal the operation will, therefore, be terminated. If, however, a complete analysis is required, proceed as follows:—

Prepare a roughly standard solution of sulphuric acid (which has been distilled from sulphate of ammonium). Of this solution, in 200 or 300 c.c. of water, take a sufficient quantity to dissolve about double the amount of the mixed iron and zinc which are supposed to be present.* Boil the acid liquid to completely expel the air, and cool it in a flask, which should be almost full and well corked. Then introduce into it the platinum or porcelain boat containing the oxide of zinc and the reduced metals. The oxide of zinc quickly dissolves, together with the iron, the solution of which is facilitated by the presence of the metallic copper. The copper and lead remain. The flask must be frequently shaken, so as to diffuse these metals throughout the liquid, and the whole is allowed to stand for some hours; the clear liquid is then carefully decanted, and the metals washed with boiling water. During this operation a trace of copper or lead may,

* It is a good plan always to weigh the reagents used in analysis, or, at all events, to ascertain approximately the quantities taken.

perhaps, get into solution in the form of sulphate, through the action of the air, or be carried over mechanically. This may be ascertained by adding to the solution a few drops of a clear solution of sulphuretted hydrogen, and heating. If brown flocks are deposited, separate them by decantation and add them to the metals.

The solution only contains the sulphates of zinc and iron; evaporate to dryness, heat the sulphates to a temperature of about 400° C., and weigh. If no iron is present, the amount of zinc present may be calculated at once. This method of estimating zinc is very accurate. If iron is present it may be separated from the zinc by methods given on p. 126. The author, however, recommends the following process:—

Calcine the sulphates in a muffle to reduce them to the state of oxides. Weigh and then moisten them with strong nitric acid until the zinc has all dissolved; evaporate to dryness and heat gently on a sand-bath until nitrous vapours cease to appear; the nitrate of iron will then be decomposed. Boil out with solution of nitrate of ammonium containing a few drops of ammonia, which will only dissolve the zinc. Wash by decantation, and weigh the residual oxide of iron, whose weight will, at the same time, enable the weight of the oxide of zinc associated with it to be calculated. The nitrates of zinc and ammonium may, moreover, be evaporated to dryness and decomposed by heat, when the residual oxide of zinc can be weighed, but this is an unnecessary operation.

The mixture of copper and lead (to which has been added the trace of sulphides which may have been separated from the sulphuric solution of the iron and zinc), may be separated by the process given at p. 216. Or the following process, recommended by Deville, may be employed:—Dissolve the mixture in sulphuric acid containing a little nitric acid; the solution, more or less turbid from the presence of sulphate of lead, is evaporated to dryness on a sand-bath, and heated to about 400° C. Weigh the mixed sulphates, and extract the sulphate of copper with water. Sulphate of lead will remain, the weight of which subtracted from the total weight of the sulphates, gives the sulphate of copper.

Separation of Tin from Tungsten.

Stannic and tungstic acids may be separated by igniting the mixture with sal-ammoniac, when the tin will be completely volatilised in the form of chloride, whilst the tungstic acid remains unchanged. As the conversion of stannic acid into volatile chloride of tin requires a long time, the treatment of the mixture, with six or eight times its weight of sal-ammoniac, must be repeated several times, until no further loss of weight is observed. Great care must be taken that the outside of the porcelain crucible and cover does not become covered with stannic acid, which may be formed

afresh from the chloride and atmospheric moisture. Hence the smaller crucible should be placed in a larger one similarly covered, and heated to a tolerably high temperature. The residue of tungstic acid becomes coloured green, then blackish. When heated in the air it assumes its usual yellow colour, and its weight is then constant.

Another satisfactory method of separating tin from tungsten has been described by Mr. J. H. Talbott.

The method is based on the fact that oxide of tin is reduced by cyanide of potassium with great facility; while tungstic acid undergoes no reduction, even when heated with the cyanide at a high temperature. The oxides of tin and tungsten are to be heated in a porcelain crucible with three or four times their weight of commercial cyanide of potassium previously fused, pulverised, and thoroughly mixed with the two oxides. The mass is kept fused for a short time, when the tin separates in the form of metallic globules, while the tungstic acid unites with the alkali of the cyanate and carbonate of potassium present. After cooling, the mass is to be treated with hot water, which dissolves the alkaline tungstate and other salts, and leaves the tin as metal; this is to be separated by filtration, washed, dried, and weighed as oxide of tin, after oxidation in the crucible with nitric acid. The tungstic acid may be estimated by difference, or be precipitated by protonitrate of mercury, after boiling the solution with nitric acid to decompose the excess of cyanide of potassium present, and then re-dissolving the precipitated tungstic acid by means of an alkali.

Commercial Analysis of Tin Ware.

The chief drawback to the analytical processes used in investigating the composition either of utensils of block tin or of thin layers of tin covering other metals, such as copper and iron, is the excessive weight of the metal to be operated on recommended in special treatises on the subject.

The following process of analysis, devised by MM. Millon and Morin, has been found to be free from the objections attaching to the ordinary method of analysis with nitric acid.

In a small flask of from 80 to 100 c.c. capacity, furnished with a disengaging tube, put about 1½ grms. of the tin, taking care to reduce the metal to fine grains, if it be not already divided by scraping; nearly fill the flask with pure fuming hydrochloric acid; adapt to the disengaging tube a bulb tube containing a solution of chloride of gold, and supplement this apparatus with another bent tube plunged into mercury.

The reaction commences in the cold, with a slight effervescence, goes on spontaneously, and ceases in about twenty-four hours. The presence of antimony or arsenic greatly favours the gaseous disengagement; scraped tin is usually more easily attacked than granulated tin.

The evolved gas traversing the bulb tube is composed of a mixture of hydrogen and arseniuretted hydrogen; all the arsenic escapes in the latter form, unmixed with antimoniuretted hydrogen; it remains in the chloride of gold, where the arsenic acid is to be sought for and estimated, in the usual manner.

When the proportion of arsenic is considerable, the gaseous disengagement becomes so rapid that one bulb tube is insufficient to arrest the arseniuretted hydrogen; but this never happens in the analysis of tin-ware used for domestic purposes; traces only of arsenic are found in this tin, at the most a few thousandths. However, if in an exceptional instance the amount of arsenic exceeds these limits, the difficulty is overcome by operating on a much less weight of alloy, and using hydrochloric acid diluted with about a fourth of its volume of water.

Antimony and tin alloy resists fuming hydrochloric acid when the antimony is in the proportion of 25 to 30 per cent. The alloy must then be melted with a given quantity of fine tin, or to facilitate the action of the hydrochloric acid, nitric acid is added to it drop by drop; the antimony is then precipitated by tin, in presence of a large excess of hydrochloric acid.

When the action of the hydrochloric acid ceases, and no more gaseous bubbles are given off, a more or less abundant black powder is seen at the bottom of the flask, containing all the antimony existing in the tin. This antimony is free from arsenic, but retains the copper. There should also be found the bismuth, which is frequently mentioned by analysts, but which the authors have never once been able to detect.

The copper remains in the black powder, except when it exists in larger proportion in the alloy than 20 per cent.

The black powder also occasionally contains traces of iron, but this is so slight in quantity that its presence may pass unnoticed.

The supernatant acid liquid is decanted, the black powder washed with distilled water, and the lixivium and acid liquid mixed. After being well washed the powder is attacked by weak nitric acid (with concentrated acid the reaction is so energetic as sometimes to ignite the powder). The excess of nitric acid is got rid of by boiling, and the residuum, containing antimony and copper, is evaporated to dryness, and slightly calcined over a lamp.

The residuum is dissolved in water acidulated with nitric acid, which dissolves the oxide of copper, but takes with it a little antimony. If calcined in too hot a flame the oxide of copper cannot be separated from the antimonic acid. Any bismuth existing in the alloy would be found with the copper in the nitric solution.

This process for separating antimony and copper is not quite perfect. If greater accuracy is desired it may be effected by pouring pure fuming

hydrochloric acid on the black powder, then boiling, and afterwards adding carefully, drop by drop, a saturated solution of chlorate of potassium; the powder dissolves, and the copper and antimony are then separated by the addition of an excess of sulphide of potassium, in which the sulphide of antimony alone dissolves, the sulphide of copper remaining insoluble.

The hydrochloric liquid decanted from the black powder, and mixed with the washing water is now to be examined. This liquid holds tin in solution, together with lead, iron, and zinc; and in it we must also look for the exceptional presence of cadmium, cobalt, and nickel.

The hydrochloric liquid is diluted with several times its volume of water, and a current of sulphuretted hydrogen is directed through it; the lead and tin are precipitated, the iron and zinc remaining in solution. Were the other metals present, the cadmium would be precipitated with the lead and tin, while the nickel and cobalt would be found with the iron and zinc. But the three exceptional metals, cadmium, nickel, and cobalt, need scarcely be taken into account, as their presence has only once been detected, and then in insignificant proportion.

The lead and tin precipitated as sulphides are moistened, at a moderate temperature, by sulphide of ammonium in excess; the sulphide of lead remains insoluble; it is washed, oxidised by nitric acid, and weighed in the state of sulphate. The sulphide of tin, completely dissolved in the sulphide of ammonium, is precipitated by weak hydrochloric acid, then collected, dried, calcined in the air, moistened with nitric acid, and re-heated before being weighed.

After the separation of lead and tin, iron and zinc are searched for in the liquid, through which a current of sulphuretted hydrogen has been passed. This liquid is evaporated to dryness and dissolved in hydrochloric acid; the iron is peroxidised by a little nitric acid, again evaporated, re-dissolved by hydrochloric acid, and to the hot liquid ammonia in excess is added, to precipitate the oxide of iron. The zinc in the filtered liquid now remains to be precipitated. The solution is brought near the boiling-point, and carbonate of sodium in excess is added drop by drop, which precipitates all the zinc. The iron and zinc in the solution may also be separated by methods described at p. 126.

ARSENIC.

Purification of Metallic Arsenic.

In order to restore to this metal its bright aspect, and to remove any slight coat of suboxide which may adhere to it, the metallic arsenic should be boiled for a few minutes in a moderately-strong solution of bichromate

of potassium, slightly acidified with sulphuric acid. The metal is next washed with water, and then with alcohol or ether, and lastly placed in a small tube closed at one end, and sealed immediately after.

Detection of Arsenic by Marsh's Test.

When distilled magnesium, as now commonly met with in commerce, is introduced into a solution containing arsenic acidulated with sulphuric or hydrochloric acid, the arsenic is entirely separated in the form of arseniuretted hydrogen. Magnesium possesses great advantages over zinc for toxicological purposes. It is now met with in commerce almost absolutely pure, and the original materials and processes of its manufacture quite remove the poisonous metals most dreaded by chemists—copper, lead, mercury, arsenic, antimony, &c. It is met with in the form of long slight ribbons, well fitted for delicate laboratory experiments. It keeps well in ordinary air. Its low equivalent displaces the ordinary poisonous metals by relatively small proportions of the precipitating metal, and the perfectly harmless character of the salts of magnesium, added to the fact that it is a normal constituent of the animal body, render its introduction into suspected fluids a matter of no consequence.

There is one precaution which must be taken in using magnesium in Marsh's apparatus. Magnesium which contains silicium gives off on contact with acids siliciuretted hydrogen, which decomposes at a dull red heat like arseniuretted and antimoniuretted hydrogen, leaving a dark brown deposit. The formation of this deposit might give rise to an error. A few words will answer this objection.

1. The magnesium which is now manufactured gives no foreign deposit in Marsh's apparatus; no sample of magnesium ribbon (as it is made for burning) yet tested has given either rings or spots. The hydrogen it gives off has always appeared remarkably pure and inodorous; its flame is hardly visible.

2. Marsh's apparatus fed by magnesium is tested under precisely the same conditions as when fed by zinc. The suspected liquids are only introduced into the apparatus after the preliminary verification of the gas-producing agents.

3. The deposit of silicium left in the red-hot tube by the passage of the hydrogen accidentally charged with siliciuretted hydrogen, is, moreover, clearly distinguishable from the deposits of arsenic and antimony. These last two disappear immediately on contact with a drop of nitric acid or aqua regia; the ring and spot of arsenic disappear suddenly when touched with a dilute solution of a hypochlorite. These three tests have no effect on the deposits of silicium produced in the tube of the apparatus.

If the suspected liquids contain no trace of arsenic or antimony, they

may contain other poisonous metals, such as copper, lead, mercury, zinc, &c. In this case the metals are found as flakes, powder, or sponge, either at the bottom of the flask of the apparatus or on the surface of the plates of magnesium. To render the precipitation complete, the liquids must be kept in a proper state of acidity, and the experiment prolonged till the new plates of magnesium introduced into the liquid dissolve, whilst retaining their metallic brilliancy. To ascertain the end of the operation, it is well to take out at first a small portion of the liquid of the flask, to put it into a small test-tube, and to introduce a well-cleaned ribbon of magnesium. However it may be, it is always necessary to leave in the flask a small excess of magnesium before pouring the liquid on a filter. All that is in suspension—corroded plates of magnesium, powder, flakes, or metallic sponge—is washed on the filter until the washings show no acid reaction; the filtered liquids should not precipitate on the addition of hydrosulphuric acid. The filter being dried, collect the deposit it contains, and analyse it in the ordinary way to ascertain the metals precipitated by the magnesium.

Improvement in Marsh's Apparatus.—Every one who has experimented with an extemporised Marsh's apparatus has found that, after the gas has burned a short time, the glass tube has become fused and the aperture closed. This may be prevented by platinising the extremity of the tube. Draw out the tube, file it to make it a little rough, and then dip it into a strong solution of bichloride of platinum, so as to take up a drop or so. Then carefully heat the point until it acquires a beautiful metallic lustre. By repeating this four or five times a good coating of platinum is obtained both outside and inside.

Reinsch's Test for Arsenic.

This process consists, as is well-known, in extracting arsenic from its hydrochloric solution, by means of metallic copper. The black deposit which results is usually regarded as pure arsenic. M. Lippert has shown that this deposit contains only 32 per cent of arsenic, the remainder being copper. This is a true alloy, of a definite and constant composition, having the formula Cu_5As.

When heated in a hydrogen current, this black powder loses a little arsenic, and is transformed into a white, silvery alloy, oxidising slightly in the air, agreeing in its composition, Cu_6As, with *Domeykite*, a mineral found at Copiabo. The great sensitiveness of Reinsch's process arises, then, from the large proportion of copper allied with the deposited arsenic. It must, however, be remembered that all the arsenic will not be volatilised by heating in a hydrogen current, and that at least half will remain in the deposit. (See also Separation of Arsenic from Copper.)

Identification of Arsenious Acid by Crystallisation.

By allowing the crystals of arsenious acid to form very gradually by slow cooling, they can be obtained very large and perfect. The following mode of forming them is the one recommended by Dr. F. W. Griffin :—Drive the substance entirely off the lower half of the tube, which is made very hot by waving it about in the flame. Then re-vapourise the sublimate, holding the tube (which should be closed by a loosely-fitting cork) as upright as possible. The dense vapour sinks to the bottom, and will give large and regular crystals as the glass slowly cools. These crystals glitter in the sun like diamonds, and exhibit the same play of colours; they are from the 150th to the 200th of an inch in diameter, and under an inch objective form specimens for the micro-crystallographer. Here and there we find octahedra absolutely perfect, but they are more frequently truncated; all the angles, however, being beautifully sharp. The majority are transparent, but some are only translucent, or even opaque. By reflected light (using a bull's-eye condenser) they appear, in consequence of their adamantine lustre, like diamonds lying in high relief on a black ground; but their complete shape is most strikingly displayed by a combination of strong reflected and feebler transmitted rays of various degrees of obliquity. A tube of half an inch in diameter, under a one-inch objective, presents nearly the entire field in focus, and the perfect crystals appear from one-half to three-quarters of an inch in diameter.

Nitrate of Silver Test for Arsenic Acid.

Arseniate of silver is slightly soluble in an aqueous solution of nitrate of ammonium, and readily soluble in both ammonia and dilute nitric acid; it is, therefore, not easy to detect small quantities of arsenic by means of nitrate of silver, as usually employed, unless the test be applied with extreme care. Mr. Every has found that the addition either of acetate of sodium, acetate of ammonium, or Rochelle salt, to a mixed solution of arsenic and nitric acids, is sufficient to ensure the immediate precipitation of arseniate of silver when ammonio-nitrate of silver is introduced. Instead of the acetates or tartrates, recently precipitated carbonate of silver may be employed to neutralise free nitric acid. When present in relatively large quantity, arsenic acid readily precipitates silver from a solution of nitrate of ammonium and ammonio-nitrate of silver, but the colour of the precipitate is uncertain.

Detection of Arsenic in Commercial Hydrochloric Acid.

When arsenious or arsenic acid is dissolved in fuming hydrochloric acid, and a solution of protochloride of tin dissolved in hydrochloric acid is added thereto, a brown-coloured, very bulky precipitate is formed, which rapidly

settles down. After having been collected on a filter and washed, first with hydrochloric acid, and then with water, to remove the acid, and then dried over sulphuric acid *in vacuo*, the precipitate forms a greyish coloured powder, of metallic aspect; this, on being rubbed in an agate mortar, exhibits metallic lustre, and partially volatilises on being heated, while oxide of tin, in the shape of a very light powder, is left. The precipitate consists of from 98·46 to 95·86 per cent of metallic arsenic, according as arsenious acid, arsenic acid, or arseniate of ammonium and magnesium has been employed. The precipitate is never obtained quite free from tin. When the hydrochloric acid employed has a sp. gr. of 1·115, the arsenious or arsenic acid dissolved therein becomes for the most part converted into chloride of arsenic; and the reaction, therefore, takes place between that chloride and protochloride of tin. When the hydrochloric acid has a sp. gr. of 1·100, the arsenious acid is not converted into chloride of arsenic, but is dissolved as arsenious acid. Chloride of tin does not act upon combinations of antimony under the same conditions.

In order to eliminate all arsenic from it, crude hydrochloric acid, sp. gr. 1·104, should be treated with a strong solution of protochloride of tin in pure hydrochloric acid, left standing for twenty-four hours, and the precipitate removed by filtration. The acid is next placed in a retort, the first 1-10th of the distillate kept separately, and the remainder distilled off to dryness, when that portion will be found absolutely free from arsenic; the first 1-10th may in some cases, retain as much as 0·02 per cent of arsenic.

Estimation of Arsenic in Tersulphide of Arsenic.

To determine the arsenic contained in tersulphide of arsenic—an operation often necessary for the estimation of arsenic—M. Graebe uses a standard solution of iodine, as in the estimation of arsenious acid. Suspend the sulphide of arsenic in water, add some carbonate of sodium, then a little starch paste, and the standard solution of iodine. It is necessary that the sulphide of arsenic should be freed from sulphuretted hydrogen. For every equivalent of tersulphide of arsenic converted into arsenic acid, five equivalents of iodine are decolourised by conversion into hydriodic acid, and three equivalents of sulphur are precipitated.

Estimation of Arsenic in Pentasulphide of Arsenic.

A solution of pentasulphide of arsenic in sulphide of ammonium, instantly yields a precipitate of ammonio-arseniate of magnesium by a solution of magnesia. Lenssen states that the sulphides of tin and of antimony are not precipitated under the same conditions. Attempts to found a process of separating arsenic from tin and antimony on this reaction have proved unsuccessful.

Estimation of Arsenic in Ores.

For estimating the amount of arsenic in ores, Mr. Parnell says that the neatest, simplest, and most accurate mode of procedure is to heat the finely-divided sample in a gentle stream of chlorine gas to a temperature of about 200° C., and to collect the escaping chloride of arsenic in chlorine-water. If free from antimony, the liquid may be well boiled, to expel free chlorine, and the arsenic precipitated with sulphuretted hydrogen, and weighed as pentasulphide.

In cases where the arsenic is obtained in the form of arsenio-magnesian phosphate (as in separation of the metal from antimony or copper), the most accurate plan would be to dissolve the precipitate in hydrochloric acid, and precipitate the arsenic as pentasulphide. When the amount of arsenic is small, it may be weighed as the double arseniate. The sample should not, however, be dried at a higher temperature than that of an ordinary water-bath—namely, about 95° C. Perfectly accurate results could, no doubt, be obtained by drying the precipitate over sulphuric acid, when it retains its six equivalents of water. The only objection is that it would take many days for a filter containing a precipitate to be properly dried by this means.

Separation of Arsenic from Tin.

Bisulphite of potassium dissolves sulphide of arsenic, but does not dissolve sulphide of tin. The mixture of the two sulphides, oxidised by nitric acid, is allowed to digest with sulphur and caustic potash till solution is complete (or till the formation of a metallic oxysulphide, which is separated by filtration). The liquid, treated by excess of sulphurous acid, is allowed to rest for some time, and is then evaporated till two-thirds of the water and all the sulphurous acid have gone off. Filter off the sulphide of tin, and wash it, not with water, which must not be used here, but with a concentrated solution of chloride of sodium. This may be removed from the precipitate by means of a slightly acid solution of acetate of ammonium, but the liquor so obtained must not be added to the washing waters charged with salt. The sulphide of tin, when dried, may be converted into oxide of tin by roasting in contact with air. The arsenic which the liquid contains in the state of arsenious acid may be precipitated by a current of sulphuretted hydrogen.

The sulphides of arsenic, even upon very long boiling with oxalic acid, are almost unattacked. Very minute traces of the metal sometimes go into solution, but may be re-precipitated by a bubble or two of sulphuretted hydrogen. Accordingly, the presence even of an enormous excess of oxalic acid does not hinder the precipitation of arsenic as sulphide. Both sulphides of tin, if moist and freshly precipitated, are readily decomposed

by moderately-long boiling with an excess of oxalic acid, sulphuretted hydrogen being given off. To separate the two metals proceed as follows:— To the solution containing arsenic and tin (this solution being prepared in the usual manner for the precipitation of the sulphides) add oxalic acid, in the proportion of about 20 grms. of the reagent for every gramme of tin, taking care to have the whole so concentrated that the acid will crystallise out in the cold. Then heat to boiling, and pass in sulphuretted hydrogen for about twenty minutes. No precipitate appears at first; but, as soon as the liquid is saturated with the gas, sulphide of arsenic begins to fall, and, in a very few moments, is completely thrown down. Then, as usual, the whole should be allowed to stand about half-an-hour in a warm place, before filtering. Every trace of arsenic is precipitated, so that, in the filtrate from the sulphides, it cannot be discovered by Marsh's test. The precipitated sulphide of arsenic is absolutely free from tin.

Separation of Arsenic from Antimony.

An accurate method of separating these two bodies is founded on the fact that recently precipitated sulphide of arsenic is soluble in bisulphite of potassium, while sulphide of antimony is insoluble. If, for example, we have to analyse commercial grey sulphide of antimony, or metallic antimony, it can be done as follows:—Mix the finely-pulverised and weighed substance with a little sulphur, and digest in a solution of protosulphide of potassium; the mass dissolves, generally leaving a black residue, consisting of a mixture of sulphides of lead, iron, and copper, which must be filtered off and examined separately. The liquid is mixed and digested with a large excess of water saturated with sulphurous acid, then heated and kept in ebullition till two-thirds of the water has boiled away and there is no smell of sulphurous acid. Sulphide of antimony will be precipitated, and from the filtrate from this the arsenic may be precipitated by a stream of sulphuretted hydrogen gas.

Tartar emetic has sometimes been found to contain arsenic. This impurity may be detected in the following manner:—2 grms. of the suspected tartar emetic are reduced to a fine powder and dissolved in 4 grms. of pure hydrochloric acid (sp. gr. 1·124). The glass vessel wherein this solution is made ought to be narrow, and capable of being well closed, and of sufficient size to contain an additional quantity of at least 30 grms. of hydrochloric acid. A quantity of pure hydrochloric acid should be thoroughly saturated with sulphuretted hydrogen gas, and of this acid at least 30 grms. are added to the solution of the tartar emetic. The glass vessel containing the solution is well corked, and, after having been shaken up, set aside; the turbidity which at first appears soon subsides (if it does not do so, it is due to the too great saturation of the hydrochloric acid with

sulphuretted hydrogen, and should be remedied by the addition of pure hydrochloric acid). If no arsenic is present, the liquid remains colourless; but the slightest trace of arsenic gives rise to a yellow colouration, and soon after to a perfectly perceptible pure yellow precipitate of sulphide of arsenic.

Among the many methods for separating arsenic from antimony, the one which is based upon the dissimilar deportment of arseniuretted and antimoniuretted hydrogen with nitrate of silver, deserves to be favourably mentioned; the former, yielding arsenious acid, which passes in solution; the latter giving rise to the formation of antimonide of silver, which is insoluble in water. The arsenic may be recognised in solution by ammonia, if there be an excess of silver, or by sulphuretted hydrogen, if the silver has been entirely precipitated. By boiling the mixture of silver and antimonide of silver, after the arsenious acid has been carefully washed out by boiling water, with tartaric acid, this dissolves the antimony alone, and the solution thus obtained yields at once the characteristic orange-yellow precipitate with sulphuretted hydrogen.

With minute quantities this process proves successful, inasmuch as 5 milligrammes of either metal in the presence of 100 times the amount of the other can be satisfactorily exhibited. In evolving the hydrogen-compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence of even moderate quantities of this acid greatly interferes with the free disengagement of the gases. It is also preferable to employ magnesium instead of zinc for this purpose (see p. 257).

Detection of Arsenic in Bismuth.

Subnitrate of bismuth occasionally contains arsenic. This may be detected in the following manner:—About half a grm. of the subnitrate is placed in a test-tube, and one c.c. of pure and concentrated sulphuric acid is next added, to expel the nitric acid. After this has been driven off, the tube being kept in a vertical position, from 4 to 5 c.c. of pure hydrochloric acid are added, and when the liquid has become quite clear, about 1·5 to 2 grms. of pure protochloride of tin. After this salt has been dissolved, about 3 c.c. of strong and pure sulphuric acid are added; and, if the mixture does not then become very hot, it is heated just to the boiling-point. If no arsenic is present, the liquid remains clear and colourless, even after standing for some time; but if even a trace of arsenic is present, the fluid becomes at first pale yellowish, next brownish coloured, and at last metallic arsenic is deposited as a deep greyish brown flocculent substance. Even when the arsenic is present with the bismuth in the proportion of one to half a million, a colouration ensues.

Separation of Arsenic from Copper.

Mr. E. W. Parnell has carried out some accurate experiments on the best means of separating these metals.

Separation by Treatment of the Mixed Sulphides with Sulphide of Sodium.—To a mixture of the two metals excess of hydrochloric acid is added; the metals are then thrown down by sulphuretted hydrogen, the mixed sulphides introduced into a flask, covered with a colourless solution of sodium sulphide, and maintained at a gentle heat on the water-bath for about twelve hours. The liquid is then filtered off, the filtrate separated, and the sulphide of copper on the filter washed with boiling water, to remove every trace of soluble arsenic. The sulphide of copper is then dissolved in nitric acid, the solution evaporated with a small quantity of sulphuric acid, the residue dissolved in water, again treated with sulphuretted hydrogen, the precipitate treated as before with perfectly pure sulphide of sodium, and filtered. The clear solution (that will contain any arsenic that has remained with the copper in the first instance) is decomposed with hydrochloric acid, the precipitated sulphur collected, washed, and treated with ammonia, which will dissolve any sulphide of arsenic that may be mixed with it. A little carbonate of sodium is added to the ammoniacal solution, and the liquid evaporated to dryness in a small porcelain dish, the residue mixed with a little potassium cyanide, and the mixture examined for arsenic, by heating it in a glass tube in a slow stream of carbonic acid. A very faint mirror of metallic arsenic is obtained, probably not exceeding 1-10th of a milligramme.

The filtrate from the first treatment with sodium sulphide is next decomposed with hydrochloric acid, the precipitate thoroughly washed and dried, and carefully sublimed. No trace of copper remains as a residue. From this, therefore, it is evident that a satisfactory separation can be effected by using a colourless solution of sodium sulphide.

As sulphide of ammonium dissolves small quantities of sulphide of copper it cannot be used instead of sulphide of sodium.

Separation by means of Chlorine Gas in the Wet Way.—To a mixed solution of the metals arsenic and copper, excess of a solution of potash is added, and a slow stream of chlorine conducted into the liquid until the latter is thoroughly saturated with the gas. The mixture is then boiled, filtered, the insoluble part well washed, and the precipitate and filtrate examined respectively for arsenic and copper. The copper is perfectly free from arsenic; but the filtrate may contain a small quantity of copper (probably due to minute particles of oxide of copper being carried through the filter, as the oxide is in an exceedingly fine condition; the quantity is very small). Care should be taken to ensure a decided excess of the chlorine, or a considerable quantity of arsenic may remain with the copper.

Separation by means of Chlorine Gas in the Dry Way.—Excess of hydrochloric acid is added to the mixed solution, the metals thrown down by sulphuretted hydrogen, the precipitate thoroughly dried, placed in a small porcelain boat, and introduced into a glass tube; this latter passes through an air-bath, fitted with a thermometer to enable the tube to be maintained at a fixed temperature. This tube is allowed to project for about 4 inches beyond the air-bath. Perfectly dry chlorine is then conducted over the mixture, maintained at a temperature of about 200° C. for about half-an-hour. The projecting part of the tube, which has been almost cold during the operation, will be found to contain no trace of copper. The copper in the porcelain boat is completly soluble in weak hydrochloric acid. It is seen, therefore, from these experiments that, if proper precautions be taken to ensure perfect dryness of the mixture and the gas, a most perfect separation can be effected at a temperature of about 200° C. To avoid the formation of the globule of sulphur, or mixture of chloride of sulphur and sulphur, which often takes place in the condensing-tube, the precaution should be taken to first saturate the liquid with chlorine, or to use a solution of chlorine for the condensing liquid.

Separation by Igniting the Mixed Sulphides in Hydrogen.—This process, conducted in the usual manner, has only for its object the estimation of the copper, unless, indeed, the amount of sulphur in the mixed sulphides is accurately known, when the amount of arsenic may be calculated from the loss. To effect the separation, the mixture is introduced into a small porcelain crucible, fitted with a perforated cover and tube for conducting in the gas. A little sulphur is added, a gentle stream of hydrogen conducted into the crucible, and the mixture carefully heated by the lamp, and finally raised to bright redness. The subsulphide of copper which is left will not contain the slightest trace of arsenic.

Detection of Arsenic in Commercial Copper.

As even in the most satisfactory performance of Reinsch's test for arsenic —the deservedly favoured test of English toxicologists—there is always some, although but an extremely small quantity of the copper wire, foil, or gauze dissolved, and, as commercial copper is rarely quite free from arsenic, and sometimes contains a very notable proportion thereof, it is important that the copper to be used in medico-legal researches as a precipitant for arsenic should be specially tested as to its purity. But, as in the ordinary mode of experimenting by Reinsch's process, the amount of metal dissolved is scarcely appreciable, it is quite unnecessary to submit any considerable quantity of it to examination. If a solution of four or five grains of the copper does not yield any evidence of arsenic, it is quite pure enough for the purpose, even though a little arsenic should be recognised in the solution of a larger quantity.

As a means of detecting traces of arsenic in copper, Dr. Odling considers the following process to be superior to any hitherto proposed in conjoint delicacy and rapidity of operation:—

A few grains of the copper cut into fine pieces are placed in a small tube-retort, with an excess of hydrochloric acid, and so much ferric hydrate or chloride as contains a quantity of iron about double the weight of the copper to be acted upon. The mixture is then distilled to dryness, some care being taken at the last to prevent spirting.

The whole of the copper is in this way quickly dissolved, and any arsenic originally contained in it carried over in the form of chloride of arsenic, which may be condensed in a little water with the excess of aqueous hydrochloric acid. The resulting distillate is then tested for the presence of arsenic, by treating it with sulphuretted hydrogen, or, preferably by boiling in it a fresh piece of clean copper foil or gauze. In some cases the residue left in the retort may be treated with a little fresh hydrochloric acid, again distilled to dryness, and the distillate collected and tested along with that first produced.

Most oxygenants other than ferric chloride are objectionable, as by their reaction with hydrochloric acid they give rise to free chlorine, which passes over with the distillate, and renders it unfit for being immediately tested either with sulphuretted hydrogen or fresh copper. Cupric oxide, or chloride on the other hand, is scarcely active enough for the purpose, while the dissolution of copper in hydrochloric acid brought about by mere exposure to the air is extremely tedious.

It may be as well to add that ferric chloride is rendered quite free from arsenic by evaporating it once or twice to dryness with excess of hydrochloric acid.

TELLURIUM AND SELENIUM.

Separation of Tellurium from Selenium and Sulphur.

No difficulty occurs in separating tellurium from sulphur. In fact, although they are frequently found together in nature combined with bismuth, they are not isomorphous, and, although there is a simple relation between their combining numbers, there are but few analogies between their compounds, none of which are found to crystallise in the same system. The analogies between sulphur and tellurium would, perhaps, not have been considered obvious did not selenium form a connecting-link between the two, offering, in many respects, great similarities with the former, and, in other respects, with the latter element. Both selenium and tellurium are precipitated from tellurous and selenious acids, by means of sulphurous acid, protochloride of tin, metallic tin, and several other metals. The

difficulties arising in the separation of tellurium, selenium, and sulphur consist, therefore, in the analogies between tellurium and selenium, and between sulphuric and selenic acids.

The usual way of separating selenium from tellurium is based upon the insolubility of seleniate of barium. But the difficulties in preparing selenic and telluric acids, and the slight solubility of the tellurate of barium, make this process a very tedious one. A mixture of seleniate and sulphate of barium is sometimes separated by reducing the former in a current of hydrogen, and dissolving the selenide in hydrochloric acid.

Some years ago, Dr. Oppenheim proposed an easier method of separating these elements, based upon the different way in which they are acted upon by cyanide of potassium. Sulphur is dissolved when fused with this compound and not precipitated by hydrochloric acid. Selenium—as the writer was the first to observe—is likewise dissolved, but is re-precipitated by any acid. Tellurium not only refuses to form a tellurocyanide when fused with cyanide of potassium, but takes the place of the cyanogen therein, forming telluride of potassium, which dissolves in water, with a purple colour, and is speedily decomposed, by the action of the air, into potash and metallic tellurium. This process, however, is imperfect, on account of a slight loss, which was first ascribed to the volatility of the elements at the temperature employed. The loss, however, occurs chiefly on the side of tellurium, which, of the three elements, is the least volatile, and it is owing principally to part of the tellurium being oxidised and dissolved as tellurate of potassium.

Instead of melting the elements with cyanide of potassium, it suffices to digest them with a solution of the salt. Sulphur and selenium are thus completely dissolved. A small proportion of tellurium forms tellurite of potassium, and the rest remains in the metallic state. The separation of the elements is, therefore, conducted in the following manner:—A mixture of them, reduced to a fine powder, is boiled with a solution of cyanide of potassium in a water-bath for about eight hours. Tellurium is then collected on a filter. Selenium is precipitated in the filtrate by means of hydrochloric acid, and the second filtrate is mixed with sulphite of sodium, heated, and allowed to stand for twenty-four hours. The portion of tellurium which had been dissolved as tellurite of potassium is thus completely precipitated. It is then added to the other portion collected on the filter, dried in the water-bath, and weighed. Selenium is determined in a similar manner, whilst the quantity of sulphur present is indicated by difference.

The same method may be employed for separating selenium from metals not soluble in cyanide of potassium. But if iron, copper, or other metals are present, which form soluble compounds with the reagent, partly

precipitated by hydrochloric acid, it is necessary to dissolve the mixture of the elements in acids, and to add a quantity of sulphide of ammonium sufficient to dissolve the selenium and tellurium. They must then be precipitated from this solution as sulphides and treated with cyanide of potassium as described above. When sulphide of selenium is acted upon by cyanide of potassium, the selenium is first dissolved, and a residue of sulphur remains behind, which disappears but slowly. The red modification of selenium is dissolved more easily than the black. Selenious acid cannot be reduced by being boiled with cyanide of potassium.

Estimation of Selenium.

Sulphurous acid is the best reagent to precipitate selenium when this element exists in the state of selenious acid; the precipitation should be performed in the presence of hydrochloric acid. Sulphurous acid may also be replaced by phosphorous acid, likewise in the presence of hydrochloric acid; but the reduction takes place much slower than when sulphurous acid is used.

As pointed out above selenium may be estimated by fusing the body containing it with cyanide of potassium, dissolving the fused mass in water, and then supersaturating the solution with hydrochloric acid, which effects the complete precipitation of the selenium at the end of a few hours. The fusion ought to be performed in an atmosphere of hydrogen; it is advisable, when the substance contains free selenious acid, to previously saturate this acid with an alkaline carbonate, so as to avoid volatilising small portions before the cyanide of potassium has had time to react upon it.

The solution obtained by treating the fused mass with water contains selenocyanide of potassium, together with a small quantity of selenide; it is necessary, on this account, to boil the liquid for some time before the addition of hydrochloric acid, to convert the selenide into selenocyanide. Without this precaution, a portion of the selenium might be disengaged in the form of seleniuretted hydrogen.

When the selenium acids are fused with alkaline carbonates, in an atmosphere of hydrogen, they are reduced to alkaline selenides; from a solution of these latter a slow current of atmospheric air entirely precipitates the selenium. This process may serve for estimating selenium, but it is less accurate than the preceding.

Sulphuretted hydrogen completely precipitates selenious acid from its solutions in the form of disulphide of selenium, from the weight of which the selenium may be determined.

Selenious acid may be estimated in its aqueous solution, or, in the presence of nitric and hydrochloric acid, by simple evaporation, taking care not to exceed a temperature of 100° C., above which a portion of the acid may volatilise.

The ordinary process for the estimation of selenic acid, which consists, as is known, in precipitating this acid as a barium salt, is, according to Rose, far from deserving the confidence with which it is usually regarded. On the one hand, seleniate of barium is much more soluble than the sulphate; on the other hand, it possesses, in a much greater degree than this latter salt, the property of carrying down with it considerable quantities of the soluble salts which are contained in the liquid. It is better to reduce the selenic acid to selenious acid with hydrochloric acid, and then to precipitate the selenium with sulphurous acid.

When it is desired to estimate the selenic acid in an insoluble combination, particularly in seleniate of barium, this combination is decomposed by an alkaline carbonate; the transformation into an alkaline seleniate takes place even in the cold, and it is then easy to reduce the selenic to selenious acid by means of hydrochloric acid.

Separation of Selenium from Metals.

Selenium cannot be separated from the metals with which it is combined when the sulphides of these metals are insoluble in sulphide of ammonium, by making use of the solubility of selenium in this reagent. The insoluble metallic sulphide is almost always mixed with selenide. Most frequently, selenium may be separated from metals by heating the mixture in a current of chlorine; the chlorides of selenium are sufficiently volatile to render the separation generally easy. In acid solutions of the selenites of metals not precipitable by sulphuretted hydrogen, the selenium may be precipitated by this gas in the state of sulphide of selenium.

To estimate the alkalies and alkaline earths combined with selenium acids, it is sufficient to fuse them with chloride of ammonium. The alkali or alkaline earth remains in the state of chloride. One single fusion, or two at the most, are sufficient to drive off all the selenium.

Preparation of Selenium from Seleniferous Flue Dust.

This is a mixture of selenium and metallic selenides with soot, sand, &c., which accumulates in some of the flues leading to the leaden chambers from the burners where some kinds of pyrites are burned. With some ores at Mansfeld it contains as much as 30 or 40 per cent of selenium.

The dark coloured mass, after being first moistened with sulphuric acid, and then washed and thoroughly dried, is placed in a porcelain or luted glass retort. It is then strongly heated, the temperature towards the end of the operation approaching that at which the glass softens. Most of the selenium will now distil over perfectly pure.

The residue, consisting of selenides mixed with carbon and other impurities, should be dissolved in hydrochloric acid containing a little nitric acid,

Precipitate the iron and copper with caustic soda, filter, and precipitate the selenium in the filtrate either by saturating the liquid with sulphurous acid, or by evaporating with an excess of sal-ammoniac and heating until this begins to volatilise. The alkaline salt is then removed with water. If the selenium were precipitated by sulphurous acid before removing the copper from the liquid the precipitate would retain somewhat considerable quantities of this metal.

Detection of Sulphur in Selenium.

Dissolve the selenium in very strong nitric acid, add a little hydrochloric acid and boil. Any sulphur which may be present can then be detected by chloride of barium, as it will be in the form of sulphuric acid. Remove the excess of barium from the filtered liquid by addition of sulphuric acid, and reduce the selenium with sulphurous acid.

Preparation of Selenious Acid.

Act upon selenium with concentrated nitric acid, and evaporate the solution until selenious acid begins to sublime; the residue is dissolved in water. This solution may contain, beside selenious acid, some sulphuric and selenic acids; in order to separate these from each other, baryta water is added. Since selenite of barium is readily soluble in an excess of selenious acid, the addition of baryta water is continued until a small quantity of the fluid, having been filtered, no longer gives a permanent precipitate on the addition of more baryta water. The fluid, having been filtered, is evaporated to dryness and sublimed; the selenious acid thus obtained is quite free from selenic and sulphuric acids.

Preparation of Selenic Acid.

Selenic acid is prepared from selenious acid by dissolving the latter in water, and precipitating the solution with nitrate of silver; the insoluble selenite of silver is shaken up with a mixture of water and bromine until the latter is in slight excess. The solution, having been filtered and concentrated by evaporation, yields selenic acid, free from sulphuric or selenious acid.

Another good method of preparing selenic acid is given by Wöhler:—Saturate selenious acid with pure carbonate of copper and then pass a current of chlorine into the liquid, until the precipitate is completely dissolved. The solution after being again saturated with carbonate of copper is concentrated by evaporation; the seleniate of copper is then precipitated by alcohol, in which the chloride of copper dissolves. Wash the seleniate of copper with alcohol, then dissolve in water and remove the copper by a current of sulphuretted hydrogen.

CHAPTER X.

GOLD, PLATINUM, PALLADIUM, IRIDIUM, OSMIUM, RHODIUM, RUTHENIUM.

GOLD.

Detection of Minute Traces of Gold in Minerals.

The large number of non-auriferous or but slightly auriferous specimens of quartz and pyrites which have sometimes to be examined for gold renders it desirable that some quicker, less laborious, and, if possible, more exhaustive, method of analysis than the current one (that by amalgamation) should be employed. After many experiments, Mr. Skey, Analyst to the Geological Survey of New Zealand, has devised a plan which gives very good results, even when small quantities of mineral are operated on. He employs iodine or bromine for the purpose of dissolving out the gold. Both of these substances differ from chlorine especially in their relatively feeble affinities for hydrogen, so that there is less to fear that from the generation of hydrogen acids any great preponderance of other matters would be dissolved along with the gold. Either of these substances can be safely and advantageously employed for the separation of gold from its matrix.

The following particulars of experiments made in this method will be useful in showing what is approximately the smallest quantity of gold that can be positively separated and identified, when operating upon a limited quantity.

1st. 2 grms. of roasted "buddle headings" from a quartz mine at the Thames, N.Z., known to contain gold at the rate of 1 oz. or so to the ton, was well shaken for a little while with its volume of alcoholic solution of iodine, then allowed to subside. A piece of Swedish filter-paper was then saturated with the clear supernatant liquid, and afterwards burned to an ash; the ash, in the place of being white, as it would be if pure, was coloured purple; the colouring matter was quickly removed by bromine—a clear indication of the presence of gold. The time occupied by the whole process was twenty minutes.

2nd. 1 grm. of the same "buddle headings," mixed with such a quantity of earth as to reduce the proportion of gold present to 2 dwts. per ton, was

kept in contact with its own volume of the tincture of iodine for two hours, with occasional stirring; a piece of filter-paper was then saturated with the liquid, and dried, five times consecutively, and finally burnt off as before: in this case, also, the colour of the residual ash was purple, and it gave the reaction of gold.

3rd. 32 grms. of siliceous hematite, finely-pounded, were thoroughly mixed with precipitated gold to the amount of 2 dwts. per ton; then ignited and treated with bromine water. After two hours the solution was filtered, and evaporated to a bulk of 20 minims; this gave a good reaction of gold to the "chloride of tin" test.

4th. 100 grms. of the hematite, with precipitated gold at the rate of ½ dwt. per ton, treated as before, but this time well washed at the expiration of two hours; the washings evaporated along with the first filtrate, gave a fainter, but still decided, reaction of gold to the same test.

5th. Iodine, as tincture, substituted for bromine in Experiments 3 and 4, gave similar results; the only variation made was, that as a precautionary measure allowing for its slower action, they are kept in contact for twelve hours.

Careful experiments have been made to compare the results of the common amalgamating process with the foregoing, and it has been found that it is not certain, with the same expenditure of labour, to get reliable indications of gold, when present in less quantity than 2 dwts. per ton, operating upon about 100 grms. of material.

In summing up the results of these experiments, it appears, then, that for qualitative examinations for gold, or for quantitative determinations in certain cases, iodine and bromine are each superior to mercury. It also appears that a proportion of gold equal to ½ dwt. per ton, upon a bulk of 100 grms. (about 4 ozs.) of ferruginous matters, can be easily and rapidly detected. Of course, by operating upon larger quantities, gold could be discovered by this process, were it present in far less quantities, but this is sufficiently near for the majority of cases.

These processes are especially adapted for the separation of gold from sulphides, as the preliminary roasting is extremely favourable to them, the loss in the substitution of oxygen for sulphur amounting to 25 per cent by weight, while the volume remains constant (or nearly so); hence there is a corresponding porosity in the product, by which every particle of it is thrown open to contact with the solution. This mechanical accessibility obviously cannot be taken advantage of by mercury.

With sulphides these processes are practically exhaustive, while, at the same time, the simultaneous extraction of other matters is so trifling, that the proper tests for gold can be safely applied directly to the concentrated solution. In the roasting of pyrites it is necessary to raise the temperature

towards the end to a full red heat, in order to decompose the ferruginous sulphates, since if these remained iron would get into the solution. In the case of an excess of carbonate of calcium being present, it is proper to gently re-ignite the roasted mineral, &c., with carbonate of ammonium, or much lime might get into the iodine or bromine solution. On the other hand, a very high temperature is to be avoided, for a considerable quantity of fine gold can escape detection in this way, by the partial vitrification of the more fusible of the silicates.

The identification of gold by the combustion of its salts with filter-paper, seems to promise a rapid method of estimating it, comparatively, by the aid of a series of prepared test-papers, representing gold in different degrees of dilution.

PLATINUM.

Purification of Platinum.

The tendency of platinum to alloy with other metals at a temperature far below its fusing-point is sufficiently well known to every user of platinum crucibles. It is equally well known that iron, &c., which has been absorbed by platinum cannot be removed, except superficially, by the action of hydrochloric acid for instance, nor even by heating in acid sulphate of potassium. Stas, in his memoir on the atomic weight of silver, &c., states that he purified his platinum vessels from iron by causing them to come in contact, at a red heat, with the vapour of chloride of ammonium. The process had to be repeated as often as any yellow sublimate was formed. Instead of chloride of ammonium, Mr. Sonstadt puts dry double chloride of ammonium and magnesium in the platinum vessel intended for purification. The vessel is then heated to about the fusing-point of cast-iron for about an hour. In this process not only is chloride of ammonium vapour given off for a long while with the double salt, at a temperature much above that at which chloride of ammonium alone volatilises, but when that salt is completely expelled, the chloride of magnesium remaining is perpetually being decomposed with evolution of free chlorine, and, frequently, the formation of a crystalline crust of periclase lining the crucible.

Platinum thus purified is softer and whiter than ordinary commercial platinum. The method is not only available for the removal of iron, but retrieves crucibles that have become dark coloured and brittle from exposure to gas flame, as well as crucibles that have been attacked by silicates during fusion of these with carbonate of sodium.

In his original paper on this subject Mr. Sonstadt draws attention to the extreme facility with which platinum becomes impure by heating in contact with matters containing only a very small proportion of substance capable of

attacking the metal. Thus, a platinum crucible becomes sensibly impure after prolonged ignition at a high temperature, bedded in commercial magnesia. On the other hand, a platinum crucible has been kept at a constant weight to the tenth of a milligramme over a series of intense ignitions, when the precaution has been taken to bed it in chemically pure magnesia.

Analysis of Platinum Ores.

The ores of platinum contain the following substances:—

1. Sand. The whole of the sand is never removed by washing the ore; the sand contains quartz, zirconium, chromate of iron, and, in the Russian ores, titanate of iron.

2. Osmide of iridium.

3. Platinum, iridium, rhodium, ruthenium, and palladium, combined no doubt in the form of an alloy.

4. Copper and iron which exist in the ores in a metallic state, for the iron found in the sand is not soluble in acids.

5. Gold, and, oftener than is supposed, a little silver. The latter metal is generally found with the palladium, and it is very rarely that palladium is obtained quite free from silver when it is prepared by the old processes.

MM. Deville and Debray's Method of analysing these ores is as follows:—

1. *Sand.*—To estimate the sand take a small assay crucible, or an ordinary crucible with smooth sides, and melt in it a little borax, so as to glaze the inside. Now introduce from 7 to 10 grms. of pure granulated silver, and 2 grms. of the ore, fairly taken and weighed very accurately. Over the platinum put 10 grms. of fused borax, and one or two small pieces of wood charcoal. The silver is now melted, and care must be taken to keep it for some time a little hotter than the melting-point, so that the borax may be very liquid, and may dissolve the vitreous matters which accompany the platinum and constitute the sand. The crucible is now allowed to cool, and, when it is cold, the button, which will contain the silver, osmium, platinum, and all the other metals, is detached, and if necessary digested for a time with weak hydrofluoric acid to remove the last portions of borax. It is now heated to a faint redness, and then weighed. The weight of the button subtracted from the sum of the weights of the ore and silver employed will give the amount of sand contained in the ore. It is very important to know this amount, for it represents the only matter absolutely destitute of value which the ore contains; and this simple operation may be considered the most important performed in estimating the value of an ore. It is, besides, performed so quickly that it is as well to do at the same time two or three specimens, taken from different parts of a lot of platinum powder.

2. *Osmide of Iridium.*—Another 2 grms. of the ore weighed very accurately

are treated with aqua regia at 70° C. until the platinum is entirely dissolved. The aqua regia must be renewed occasionally for 12 or 15 hours, or until it is no longer coloured. It is best to perform this operation in a large beaker, and to place a cover over it to prevent loss. The solutions must be decanted with the greatest care from the metallic spangles of the osmide of iridium and the sand which remain at the bottom of the beaker. If necessary it may be filtered, but as little as possible of the osmide must be allowed to go on the paper. The insoluble residue must be washed by decantation, then dried and weighed, after having added what remained on the filter. By subtracting the weight of this residue from the weight of the sand obtained in the former operation, the weight of the osmide of iridium is obtained.

The button obtained in determining the sand might be employed in this operation. In that case it is necessary to dissolve out the silver with nitric acid, and then proceed with the residue, as just directed.

3. *Platinum and Iridium*—The solution in aqua regia obtained in the last operation is evaporated to dryness at a low temperature, and the residue is re-dissolved in a small quantity of water (if it should not entirely dissolve in the water some more aqua regia must be added, and the evaporation repeated), to which is added about twice its bulk of pure alcohol; lastly add a great excess of sal-ammoniac in crystals. The whole is now slightly warmed to complete the solution of the sal-ammoniac; it is then stirred, and afterwards set aside for twenty-four hours. The orange-yellow, or even reddish-brown, precipitate which is formed, contains most of the platinum and the iridium, but some remains in the solution. The precipitate must be thrown on a filter, and washed with alcohol. Afterwards the filter is dried in a platinum crucible, placed, for greater safety, within a larger one, and afterwards heated by degrees to low redness. The crucibles are now uncovered, and the filter is burnt at the lowest possible temperature. Once or twice after the incineration of the filter a piece of paper saturated with turpentine should be introduced into the crucible, by which means the oxide of iridium will be reduced, and the expulsion of the last traces of osmium will be effected. The crucible is now heated to whiteness until it no longer loses weight, or the reduction is finished in a current of hydrogen.

The liquid separated from the platinum-yellow by filtration is evaporated until the chloride of ammonium crystallises in large quantity. It is allowed to cool, is then decanted, and on a filter is collected a small quantity of a deep violet-coloured salt, which is the ammonio-chloride of iridium, mixed with a little of the platinum salt. This is first washed with a solution of sal-ammoniac, and then with alcohol. The salt is then ignited, and, if necessary, reduced by hydrogen like the platinum salt. The mixture of platinum and iridium, obtained by the two reductions, is then weighed. The

two metals are now digested, at about 40° or 50° C., in aqua regia, diluted with about four or five times its weight of water—the aqua regia being renewed until it is no longer coloured. The residue is pure iridium. To obtain the weight of the platinum, the weight of the iridium is subtracted from that of the mixture of the two. This method of separating the two metals is very accurate if the aqua regia used be weak, and the contact with it is prolonged.

4. *Palladium, Iron, and Copper.*—The liquor charged with sal-ammoniac and alcohol, from which the platinum and iridium have been separated, is evaporated to get rid of the alcohol, and then treated with an excess of nitric acid, which transforms the chloride of ammonium into nitrogen and hydrochloric acid. It is now evaporated almost to dryness. The residue is removed to a covered porcelain crucible, which is weighed with great care. When the matter is dry it is moistened with concentrated sulphide of ammonium, and afterwards dusted over with 2 or 3 grms. of pure sulphur. When dry, this crucible is placed within a larger one of clay, and surrounded with pieces of wood charcoal. The two are covered, and now set in a cold furnace, which is filled up with charcoal, and the fire is lighted at the top to avoid the projection of any matter from the crucible if it were tco quickly heated. After reaching a bright red heat, the crucibles are allowed to cool. The porcelain crucible now contains palladium in a metallic state, with the sulphides of iron and copper, and also the gold and rhodium. This mixture is moistened with concentrated nitric acid, which, after prolonged digestion at 70°, dissolves the palladium, iron, and copper, forming at the same time a little sulphuric acid. The solution of the nitrates is poured off the residue, which is washed by decantation, and the solution and washings are evaporated to dryness, and then calcined at a strong red heat. In this way the palladium is reduced, and the iron and copper pass to the state of oxides, which are easily separated from the palladium by means of strong hydrochloric acid. The palladium remains in the crucible, in which it is again strongly ignited and then weighed.

The chlorides of iron and copper are now evaporated to dryness at a temperature but little above 100° C., and are then treated with ammonia. The sesquichloride of iron, having lost nearly all its acid, has become insoluble; but the chloride of copper is readily dissolved, and may be filtered from the iron, which is washed, ignited, and weighed. The copper solution is now evaporated almost to dryness, and then mixed with excess of nitric acid, and heated to drive off the chloride of ammonium. Afterwards the nitrate of copper is ignited and weighed. The weight of the copper is always so small that the hygrometric water the oxide of copper may absorb may be neglected.

5. *Gold and Platinum?*—The residue insoluble in nitric acid is weighed

and treated with very dilute aqua regia, which takes up the gold, and sometimes, but very rarely, traces of platinum. To acertain if platinum be present, evaporate to dryness, and re-dissolve by alcohol and chloride of ammonium. If any platinum-yellow remain, it must be ignited and weighed. The difference in the weight of the porcelain crucible before and after the treatment by aqua regia gives the weight of the gold, from which, if any be found, the weight of the platinum must be deducted.

6. *Rhodium.*—The residue left in the crucible is rhodium, which must be reduced in a current of hydrogen.

Bunsen's Method of analysing platinum residues is as follows:—The residues employed contained no osmium, and were relatively rich in rhodium.

Platinum and Palladium.—It is easy to effect the almost complete separation of platinum and palladium from rhodium, iridium, and ruthenium. The original material is mixed in a Hessian crucible, with from $\frac{1}{4}$ to $\frac{1}{2}$ its weight of chloride of ammonium, heated until the latter is completely volatilised, allowed to glow gently until only the vapours of sesquichloride of iron show themselves, and then placed in a porcelain dish and evaporated to a syrupy consistency, with from two to three times its weight of raw *commercial* nitric acid. By this treatment with chloride of ammonium, the metals present not belonging to the platinum group will have been partially converted to lower chlorides, the rhodium, iridium, and ruthenium will have been rendered insoluble, and the silica present as gangue converted from a gelatinous mass to a finely-pulverulent condition, in which state it will admit of speedy filtering.

The chlorine compounds, produced by the chloride of ammonium, give, upon digestion with nitric acid, just enough hydrochloric acid to dissolve the platinum to bichloride, while the metallic copper and iron present act so far reducingly upon the palladium (in solution in nitric acid) that it remains in solution, not as bichloride, but as the protochloride, which latter is not precipitated with chloride of potassium. The mass is diluted with water, filtered, and the solution saturated with chloride of potassium, and the greater part of the platinum separated pure as platinochloride of potassium, which is washed out, first with chloride of potassium, and later with absolute alcohol (the last washings must not be added to the solution).

The filtrate is brought into a large flask (which can be made air-tight), which will not be more than half-filled with it. Chlorine gas is led into this flask, and it is, from time to time, shaken vigorously, until no further absorption of gas takes glace, when all the palladium will have separated as a cinnabar-red precipitate of palladiochloride of potassium (somewhat impure, however, from traces of platinum, iridium, and rhodium). The fluid from which these precipitates were obtained is now evaporated, not quite to dryness, with hydrochloric acid; and, upon addition of just so

much water as is necessary to dissolve out the chloride of potassium and other soluble salts (aiding the operation by rubbing with a pestle), there remains behind a dirty, yellow-coloured precipitate. This is separated by filtration, boiled with caustic soda and a few drops of absolute alcohol. Hydrochloric acid is added to dissolve the precipitate formed, and the liquid then saturated with chloride of potassium; the result is a precipitate of chemically pure platinochloride of potassium. The mother-liquid contains only copper, and no platinum metals.

The purification of the cinnabar-red precipitate of palladium is accomplished as follows:—Dissolve in boiling water, whereby a portion of the chloride dissolves, with evolution of chlorine, to protochloride of palladium. Then evaporate with 2½ times its weight of oxalic acid, and dissolve again in a solution of chloride of potassium; whereupon platinochloride of potassium remains behind, chemically pure. Wash out as before.

The brown liquid is then somewhat concentrated upon the water-bath; and, upon cooling, there separate bright green, well-formed crystals of palladio-protochloride of potassium (with some chloride of potassium), which, upon testing, proves free from the other platinum metals.

The fluid poured off from these crystals is then neutralised carefully with caustic soda, and gives a slight precipitate of copper and iron, which is filtered off. Upon adding iodide of potassium to the filtrate, all the palladium separates as iodide of palladium. To avoid adding an excess of the reagent, it is best to take, from time to time, a drop from the fluid with a capillary tube, and bring the same upon a watch-glass. As long as the precipitation is incomplete, the drop appears, upon a white background, *brown*; when complete, it is *colourless*; when the reagent is present in excess, it is *red*. This is tested for its purity by reducing it to metallic palladium, and then heating aud dissolving in nitric acid: when pure, it must dissolve completely. The whole mass is now reduced in a slow stream of hydrogen gas (whereby the iodine can be obtained again, as hydriodic acid, by absorbing with water). At last the mass must be strongly heated, to decompose slight traces of the subiodide of palladium which are formed.

The mother liquid from which all this platinum and palladium have been obtained may contain some iridium and rhodium; it is, therefore, evaporated to dryness with a little iodide of potassium, whereby a mixture of the iodides of rhodium and iridium separates. This can either be dissolved in aqua regia and the two metals separated (as will hereafter be described) by bisulphite of sodium, or it can be united with the next portion from which these metals will be obtained.

Ruthenium, Rhodium, and Iridium.—The residue from the original material which remains, after treatment with chloride of ammonium and

nitric acid, is treated as follows, to get the metals in a form adapted to further chemical treatment.

The method depends upon the behaviour of chloride of zinc to zinc. If a piece of zinc be melted, it rapidly covers itself with a stratum of oxide. If, to the melted metal, a metal like iridium be added, the oxide stratum hinders the latter from coming into contact with the zinc, even though it be pushed beneath the surface. If, however, a few grains of chloride of ammonium be given to it, ammonia, hydrogen, and chloride of zinc will be formed, which last dissolves the oxide stratum to basic chloride of zinc. The zinc below resembles mercury in lustre and mobility. As soon as the chloride has dissolved as much of the oxide as is possible for it, the oxide stratum again forms, and is instantly removed again by the addition of more chloride of ammonium. The melted zinc, strewn with chloride of ammonium, also possesses, like mercury, the property of attacking other metals, if the affinity exists of forming with them alloys. By strewing chloride of ammonium upon the melted zinc, a quiet surging is kept up, as the ammonia and hydrogen are given off. Many oxides and chlorides (among which are those of the platinum metals), when they come into contact with this atmosphere of reducing gases, and with the basic chloride of zinc, are instantly reduced and dissolved to alloys by the zinc. In making the solution, the zinc, in a porcelain dish, should be constantly rotated: the gangue remains in the basic chloride. The regulus, immediately upon solidifying, should be taken from the capsule, out of the yet-fluid basic chloride, and washed off with acetic acid until all the basic chloride is dissolved away. The gangue can be quantitatively determined by filtration and weighing. If the regulus is not immediately removed, the containing vessel will be broken, owing to the unequal expansion of the porcelain and the metal.

The best proportions for a quantitative separation are, to 1 part of the platinum metals, from 20 to 30 parts of zinc. For an ordinary separation, 7 parts of zinc are sufficient.

For the extraction of the residues remaining after the treatment with nitric acid, this method is admirably adapted. By fusing only once with zinc for two or three hours, all the platinum metals are extracted. The operation is the following:—

From 3 to 3·5 kilos. of commercial zinc are fused in a 2-litre Hessian crucible, chloride of ammonium from time to time strewn upon it, 400 grms. of residue, previously heated to faint glowing with chloride of ammonium, are added, and the temperature kept, for two or three hours, just above the fusing-point of the alloy, by adding, whenever the mass threatens to solidify, some chloride of ammonium. The mass is divided into three strata after solidification has taken place.

The outer stratum, easily broken away by a blow from a hammer, contains no platinum metals. The next contains some particles of the zinc and platinum alloy, imbedded in the basic chloride of zinc; it is porous, and not very thick. The inner stratum consists of a beautiful crystalline regulus.

To obtain the alloy from the middle stratum, it is only necessary to wash repeatedly with water; and the alloy gained is, of course, to be added to the regulus. To obtain this regulus as pure as possible, it is again fused with 500 grms. of zinc and some chloride of ammonium, then granulated in water, and the granules dissolved in fuming hydrochloric acid. The acid attacks the regulus with the greatest energy, and the solution is complete in less than an hour. The chloride of zinc can be used for the next operation.

The platinum metals are found at the bottom of the vessel, in the form of a finely-divided black powder, which is contaminated with zinc, and with traces of iron, copper, &c., from the latter. It cannot be purified with nitric acid, nor with aqua regia, for part of the platinum metals will thereby be dissolved, or, at best, so suspended in the fluid that filtration is impossible. If, however, the powder is treated with hydrochloric acid, singularly enough, all the impurities are dissolved; not only zinc and iron, but also lead and copper, dissolve readily, with the generation of hydrogen. The explanation is readily found in electrical currents produced by the contact of the metals, the stream passing from the positive zinc, iron, &c., to the negative platinum metals, hydrogen being given on the latter, and chlorine on the former, and uniting with them. The metallic powder, after thorough washing, possesses the property, upon being gently heated, of exploding weakly, and, when highly heated, with violence, the explosion being accompanied with the evolution of light; thereby neither hydrogen, nor chlorine, nor nitrogen, nor aqueous vapour are given off; and, as these are the only elements which it is possible that the metallic powder could have taken up, it must be assumed these metals are, by this treatment, converted into an allotropic condition, and that, upon heating, they return, with more of less energy, to their original condition. The powder contains, mainly, rhodium and iridium; but there are traces present of platinum, palladium, lead, copper, iron, and zinc.

It is intimately mixed with about three or four times its weight of completely anhydrous chloride of barium, and a stream of chlorine gas led over it at a tolerably high temperature. The operation is concluded when particles of sesquichloride of iron show themselves on the neck of the flasks containing the powder. These are carefully brushed away with filter-paper. Some water is now added, and the mass of the platinum metals dissolved with the evolution of heat. There remains behind

insoluble matter, which, upon reduction with hydrogen, alloying with zinc, and treatment with hydrochloric acid, furnishes ruthenium. From the solution all the chloride of barium is removed by careful addition of sulphuric acid. The platinum metals are now completely freed from all other metals by reduction with hydrogen, the temperature being, throughout the operation, maintained at nearly 100° C., by means of a constant water-bath. Platinum and palladium chiefly separate first; then mainly rhodium; and the last portions consist almost entirely of iridium. It is best to break off the operation when the fluid has assumed a greenish-yellow colour. The last portions of iridium (obtained by evaporating the solution to dryness, fusing with carbonate of sodium, and treatment with aqua regia) are added to the portion, afterward to be again rendered workable by renewed treatment with chloride of barium. The operation of reduction is hastened by concentrating the fluid; in doing which care must be taken to guard against explosion, on account of the hydrogen. The separated metals are treated with aqua regia, and the platinum and palladium thus dissolved separated from each other as already described. The traces of rhodium and iridium in the mother liquid can be removed entirely by continued boiling with iodide of potassium (whereby they precipitate as iodides); they are then dissolved in aqua regia and added to the insoluble portion.

This insoluble and partly-oxidised portion is now again reduced in hydrogen gas, treated, as before described, with chloride of barium, and, after the removal of the barium, the last traces of platinum and palladium removed by boiling with caustic soda. Rhodium and iridium now alone remain to be separated.

The brown-red fluid is, for this purpose, evaporated with hydrochloric acid, and, after filtration, treated with bisulphite of sodium in great excess, and the whole allowed to remain quietly in the cold for several days. The double sulphide of rhodium and sodium separates slowly, giving a lemon-yellow precipitate. The solution becomes lighter and lighter, and finally almost colourless. The colour of the precipitate changes with that of the fluid, becoming, with it, lighter. This precipitate, upon washing, contains the rhodium almost pure.

Upon heating the fluid gently, a yellow-white precipitate separates, which consists mainly of rhodium, but contains, also, some iridium. After filtering off this precipitate, the solution, upon being concentrated to a small volume, gives yet two precipitates—

1. A curdy, slowly-separating, yellowish-white precipitate, containing nearly chemically pure iridium, with but the faintest traces of rhodium.

2. A heavy, crystalline powder, quickly separating, which is readily freed from the first by decantation. Upon testing, it gives all the reactions for

iridium, but likewise some peculiar reactions not shown by the latter. It may possibly contain a new metal.

The complete separation of rhodium from iridium is accomplished by treating the yellow precipitates with concentrated sulphuric acid. They are brought in small portions into the acid, heated in a porcelain capsule until all the sulphurous acid has escaped, and then left upon the sand-bath until the free sulphuric acid has been driven off and the sulphate of sodium formed. Upon boiling the mass in water, all the iridium dissolves as sulphate, with a chrome-green colour; while the rhodium remains behind as a flesh-coloured double salt of sodium and rhodium. The latter is boiled in aqua regia, and washed by decantation. It is insoluble in water, hydrochloric or nitric acids, and in aqua regia. The rhodium and iridium are now completely separated.

The first yellow precipitate obtained in the cold by the bisulphite of sodium, gives, by this treatment, the rhodium quite pure. The second and third precipitates, containing much iridium, give a very fine rhodium, but still slightly contaminated with iridium. The products, therefore, obtained by this treatment with sulphuric acid (which betray their contamination with iridium by their somewhat brownish colour) are collected for themselves, the rhodium separated therefrom by glowing, treated again with chloride of barium, and the operation of separation repeated. The green solution, containing only iridium, is gradually heated over an ordinary burner, in a porcelain capsule, and, afterwards, upon the sand-bath, to remove the excess of sulphuric acid; and, finally, the capsule and its contents are highly heated in a Hessian crucible. There is formed thereby sulphate of sodium and sesquioxide of iridium. Upon boiling the mass with water, the last remains behind as a black, insoluble powder, which is readily washed by decantation.

C. Lea's Process for Analysing Platinum Ores.—The ores on which these analyses were performed contained chiefly iridium, together with ruthenium, osmium, rhodium, and platinum. It was a Californian osm-iridium which had already undergone a preliminary fusion with nitre and caustic potash.

This material is boiled with aqua regia to extract all the soluble portions, the residue then ignited with nitre and caustic soda,* and the fused mass heated with water. From the resulting solution small portions of osmite of potash crystallise out. The metallic oxides are next precipitated, and

* Attention is necessary to the order in which these substances are employed. If the caustic soda is melted first, it attacks the iron vessel strongly, and may even go through. If added last it causes sudden and violent effervescence, with danger of boiling over. Therefore, place the nitre first in the vessel, and when it is fused add the caustic soda. When a red heat is obtained add the osmiridium by degrees.

this precipitate, together with the portions insoluble in water, is boiled again with aqua regia, ignited again, &c. These ignitions still leave a small portion of unattacked residue.

The boiling with aqua regia is continued for a long time, in order to get rid as thoroughly as possible of the osmic acid. Even 200 hours' boiling, however, still leave osmium in the solution in easily recognisable, but in comparatively small, quantity. The greatest advantage is found throughout the whole of this part of the operation from the use of a blowing apparatus, with the aid of which all inconvenience from the fumes of osmic acid is avoided. The apparatus is constantly swept clear by a powerful air current, and the osmic acid is removed as fast as it is volatilised. As the ignition of the ore with alkaline nitrate and caustic alkali scarcely drives off any osmium, and as almost all inconvenience in manipulating the resulting solutions can be avoided by throwing down the metals with alcohol from the hot alkaline solution, in place of using acid, it is clear that the difficulties arising from the noxious effects of osmic acid can be almost wholly removed from each of the various stages of the process.

A very prolonged treatment with aqua regia is found to have the great advantage of converting nearly the whole of the ruthenium into bichloride. The separation of ruthenium in this form from the other metals is so easy in comparison with the difficulties presented by the separation of the sesquichloride, that this advantage cannot be looked upon as other than a very material one.

Sal-ammoniac is next added to the mixed solution in quantity sufficient to saturate it. The sandy crystalline precipitate (A) is thoroughly washed out, first with saturated, and then with dilute sal-ammoniac solution. The saturated solution of ammonium salt carries through with it nearly the whole of the ruthenium as bichloride (B); the dilute solution is found to contain small quantities of iridium, rhodium, and ruthenium (C).

Over (A), water acidulated with hydrochloric acid is placed, and allowed to stand for some days. This is treated with ammonia and boiled. The precipitate, when treated with hydrochloric acid, furnishes green chloride of osmium, with traces of ruthenium.

In these preliminary steps, Claus's process has been followed, which undoubtedly offers advantages over any other, and best brings the metals into a convenient state for separation, varying it only by prolonging the treatment with aqua regia, and converting the ruthenium principally into bichloride instead of sesquichloride.

We have now three portions of material:—(A), consisting of iridiochloride of ammonium, containing also ruthenium, osmium, rhodium, and platinum in small quantities. (The ore under examination contained no palladium,

which metal, if present, has always its own peculiar mode of separation, and does not enhance the difficulties of operation). (B), containing bichloride of ruthenium, together with iron in quantity, copper, and other base metals which may be present. Finally, (C), containing chiefly bichloride of ruthenium, mixed with small quantities of iridium and rhodium.

The next step in the process is to introduce the iridiochloride of ammonium (A) into a large flask with twenty to twenty-five times its weight of water, and apply heat until the solution is brought to the boiling-point; the whole of the iridiochloride of ammonium should be brought into solution in order that the reduction to be effected may not occupy too long a time, as otherwise the platinum and ruthenium salt, if any be present, might likewise be attacked. Crystals of oxalic acid are thrown in as soon as the solution actually boils, whereupon a lively effervescence takes place, and the iridium salt is rapidly reduced. As fast as the effervescence subsides, more oxalic acid is added until further additions cease to produce any effect. When this is the case, the liquid is allowed to boil for two or three minutes longer, not more; the heat is to be removed, and the flask plunged into cold water.

By this treatment any platinum present is unaffected. Sal-ammoniac in crystals is added, about half enough to saturate the quantity of water present. The sal-ammoniac may be added immediately before the flask is removed from the fire. After cooling, the solution should be left for a few days in a shallow basin, whereby the platinochloride of ammonium will separate out as a yellow, a reddish, or even (especially if the quantity of water used was insufficient) as a black crystalline powder, according to the quantity of iridium which it may contain.

The mother water is to be again placed in a flask, and boiled with aqua regia. On cooling, the iridiochloride of ammonium crystallises out, and any traces of rhodium and ruthenium which may be present remain in solution. The iridium salt is to be washed with a mixture of two parts saturated solution of sal-ammoniac and three parts of water, and may then be regarded as pure.

The treatment by oxalic acid affords iridium free from all traces of ruthenium. The detection of very small quantities of ruthenium in presence of much iridium has been hitherto an impossibility, or could only be effected by Claus's method of allowing a small quantity of water acidulated by hydrochloric acid to remain in contact with the iridiochloride of ammonium for some days. The ruthenium salt, by its superior solubility, tended to dissolve first; hence the acidulated water, after standing, contained ruthenium in larger relative proportion than the original crystals; the ruthenium reactions were more marked, and if it was present, and in sufficient quantity, it could be detected by sulphocyanide of potassium, or,

better, to an experienced eye, by acetate of lead. The objections to this method are sufficiently obvious.

The treatment of solutions (B) and (C) presents no difficulty. With (B) the best plan is to place the solution aside in a beaker covered with filter paper for some time. Treated in this way, the bichloride gradually crystallises out, and by re-crystallisations may be obtained in a state of perfect purity.

Solution (C) is to be evaporated to dryness, and reduced to an impalpable powder. It is then to be thrown upon a filter, and thoroughly washed with a perfectly saturated solution of sal-ammoniac. The bichloride of ruthenium is thus carried through, with perhaps a trace of sesquichloride of rhodium, from which, however, it is easily freed by crystallisation. From the residue, the sesquichloride of rhodium and ammonium is removed by a dilute solution of sal-ammoniac, perfectly free from the iridium, which is left behind.

In connection with this separation, Mr. Lea makes a remark, which, though of special reference to this particular case, is also applicable to all those cases in which the double chlorides of the platinum metals are to be separated by their various solubilities in solution of sal-ammoniac. This most valuable process, for which we are indebted, as for so much else, to Claus, whose untiring labours have made him the father of this department of chemistry, requires to be applied with some attention to minutiæ.

The crystalline matter must be reduced to the finest powder, and after being thrown upon the filter, it must be washed continuously until the separation is effected. Any interruption of the washing is followed by more or less crystallisation of sal-ammoniac through the material, which precludes an effectual separation. The same material which in a state of coarse powder will hardly yield up enough bichloride of ruthenium to colour the sal-ammoniac solution, will, when thoroughly pulverised, give an almost opaque blood-red filtrate.

Solution (C) may be subjected to a different treatment from the foregoing, and oxalic acid may be used to effect the separation. The solution is to be brought to the boiling-point, and oxalic acid added as long as effervescence is produced. The bichloride of iridium is thereby reduced, the bichloride of ruthenium and the sesquichloride of rhodium are not affected. Sal-ammoniac is then to be dissolved in the solution to thorough saturation. By standing and repose the double chloride of rhodium and ammonium separates out. The solution is then re-oxidised by boiling with aqua regia; by standing for some days in a cool place, the iridiochloride of ammonium crystallises out, and the supernatant solution contains the double chloride of ammonium and bichloride of ruthenium, which may be rendered pure by several re-crystallisations.

For purifying the double chloride of iridium and ammonium, the oxalic process is decidedly the best. It is simple and less trouble, and there is the further advantage that the platinum is left in the condition of double chloride, whereas when the usual method of treating with aqueous sulphuretted hydrogen is used, the platinum is apt to be converted partly into sulphide, together with any traces of rhodium and ruthenium which may be present. When oxalic acid is used, the platinum remains behind as a reddish powder, containing some iridium, from which it may be freed in the ordinary manner, if it is present in quantity sufficient to be worth working.

For treating a mixture such as that which is here designated as (c), containing no platinum, and only ruthenium present in the form of ruthenio-chloride of ammonium, it is unnecessary to apply reducing agents, and the first method described is the best. But if it be proposed to effect the separation by the reduction of the iridium compound, the method here described is preferable to that based on the use of sulphuretted hydrogen even in this case.

The action of oxalic acid on the platinum metals is interesting; its reducing effect upon bichloride of iridium at the boiling-point is immediate. On bichloride of ruthenium it seems to have no effect whatever, and they may be boiled together for a length of time without sensible result. In a trial made with sesquichloride of ruthenium and ammonium the oxalic acid was boiled with the metallic salt for a considerable time without any apparent effect becoming visible, but by long continued boiling a gradual precipitation took place. When platinochloride of ammonium was boiled with oxalic acid, no effect was produced for a considerable time, but gradually the platinum salt diminished in quantity, and the liquid acquired a stronger yellow colour, perhaps owing to formation of soluble platinic oxalate. This process will not, however, furnish an easy and convenient method of purifying commercial platinum from the iridium always found in it, as the reduction of very small quantities of double chloride of iridium and ammonium in the presence of a large proportion of the corresponding platinum salt is difficult and slow, and the platinum salt itself is evidently attacked.

Dr. Wolcott Gibbs's Process for the analysis of platinum ore is as follows:—The metals are first obtained in the form of nitrohydrochloric solution, and the liquid is then evaporated to dryness with an excess of chloride of sodium. The mass of double chlorides obtained as already mentioned is to be rubbed to a fine powder, introduced into a deep porcelain evaporating dish, and mixed with four or five times its volume of boiling water. A solution of nitrate of sodium is then to be added in small quantities at a time, the solution being continually stirred, and occasionally

neutralised by addition of carbonate of sodium. The liquid soon becomes olive-green, and the greater part of the mass dissolves; it is advantageous, when the quantity of the mixed chlorides is large, to pour off the liquid as soon as it appears saturated, and to repeat the operation with a fresh quantity of water. The undissolved mass, which consists chiefly of the impurities of the ore, when these have not been removed before the process of oxidation, is then to be thrown upon a filter, and washed with boiling water until the washings are colourless. By keeping the solution somewhat alkaline, the whole of the iron remains upon the filter as sesquioxide, with other impurities. The filtrate contains iridium and rhodium as sesquichlorides, ruthenium partly as bichloride and partly as protochloride, platinum as bichloride. When the operations already mentioned have been well performed, no determinable quantities of osmium and palladium are present. On cooling, the greater part of the platinum is deposited as platinochloride of potassium mixed with a little of the corresponding iridium salt, and is to be separated by pouring off the olive-green supernatant liquid. The quantity of the alkaline nitrite to be added in this process need not exceed half of the weight of the mass of double chlorides, but with a little experience it will be found unnecessary to weigh the nitrite added, the process of the reduction of the iridiochloride of potassium being evident to the eye.

To the filtrate a solution of nitrite of sodium is to be added, and the whole boiled until the liquid assumes a clear orange-colour. Nitrite of sodium should be used in this process, because the resulting double nitrite of iridium and sodium is easily decomposed by boiling with hydrochloric acid, which is not the case with the potassium salt. When nitrite of potassium is used, a small quantity of the white insoluble double salt already mentioned is usually formed and renders the solution turbid.

To the clear yellow, or orange-yellow, boiling solution, sulphide of sodium is to be added until a portion of the dark brown precipitate of the sulphides of ruthenium, rhodium, and platinum is dissolved with a brown-yellow colour, and an excess of the alkaline sulphide is, consequently, present. The liquid is then to be allowed to cool, and treated with dilute hydrochloric acid, until a distinctly acid reaction is produced. In this manner the whole of the platinum, ruthenium, and rhodium present in the solution are thrown down as insoluble sulphides. After complete subsidence, the sulphides are to be thrown on a double filter and thoroughly and continuously washed with boiling water. When the operation is carefully performed, the filtrate and washings contain only iridium. It is best to neutralise this solution with carbonate of sodium, boil a second time with a little additional nitrite of sodium, and treat as before with sulphide of sodium and hydrochloric acid. In this manner very small

additional quantities of the sulphides of platinum, ruthenium, and rhodium may sometimes be separated.

The filtrate is to be evaporated and boiled with an excess of strong hydrochloric acid, which completely decomposes the double nitrite of iridium and sodium, yielding the iridiochloride of sodium, which is very soluble in water. An excess of a pure and strong solution of chloride of ammonium is then to be added, the whole evaporated to dryness, and the dry mass washed with cold water, and then with a cold and strong solution of sal-ammoniac. There remains a mass of pure iridiochloride of ammonium, which may be advantageously rubbed to a fine powder, dissolved in boiling water, and allowed to crystallise. The resulting salt is chemically pure, and the crystals possess an extraordinary beauty and lustre. The mass of mixed sulphides, together with the filter, are to be treated with strong hydrochloric acid, and nitric acid added in small portions at a time. By the aid of a gentle heat the sulphides are readily oxidised and dissolved. After sufficient dilution, the liquid is to be filtered, the pulp of undestroyed filter-paper washed, the filtrate evaporated to dryness, the dry mass digested with concentrated hydrochloric acid, and again evaporated to dryness. The dry mass of chlorides and sulphates is to be re-dissolved in water, and the platinum, ruthenium, and rhodium precipitated by metallic zinc, after addition of hydrochloric acid. The finely divided metals, after filtration, washing, and drying, are then to be mixed with chloride of potassium, and treated with dry chlorine at a low red heat. In this manner the metals are again brought into the form of double chlorides, and the difficulties which arise from the presence of the sulphates are avoided.

The mixed double chlorides are to be boiled with nitrite of potassium, evaporated to dryness, and the soluble nitrite of ruthenium and potassium dissolved out with absolute alcohol in the manner described in speaking of the separation of platinum from ruthenium (p. 302). The ruthenium may then be obtained pure by converting it into the double chloride of mercury and ruthen-diamine (p. 303).

The mass undissolved by alcohol consists of platinochloride of potassium mixed with both the soluble and the insoluble double nitrites of rhodium and potassium. It is to be boiled with dilute hydrochloric acid, neutralised with carbonate of potassium, again evaporated to dryness, after the addition of nitrite of potassium, and again boiled with absolute alcohol, which sometimes dissolves a trace of ruthenium. The undissolved mass is then to be treated with hot water, and again evaporated to dryness, and this process repeated two or three times, so as to convert the whole of the soluble rhodium salt into the insoluble salt. The platinochloride of potassium may then, after reducing the mass to fine powder, be dissolved out by boiling water, when the rhodium salt remains pure, as a fine orange-yellow

crystalline powder. This may be dissolved in hot hydrochloric acid, evaporated to dryness with an excess of pure chloride of ammonium, and ignited in a clean porcelain crucible, when pure metallic rhodium remains as a porous mass mixed with chloride of potassium.

When the process above described has been carefully conducted, and especially when the quantity of nitrite of sodium added is sufficient, the mixed sulphides will be found to contain only platinum, rhodium, and ruthenium, and to be free from iridium. If, however, after converting the sulphides into double chlorides in the manner pointed out, iridium is found to be present, the process to be pursued is still the same so far as regards the separation of the ruthenium; the remaining mass is then to be dissolved in water with addition of hydrochloric acid, the solution nearly neutralised with ammonia, the platinum and rhodium separated as sulphides in the manner already pointed out, brought into the form of double chlorides, and then separated by nitrite of potassium as before.

For the complete success of this method it is absolutely necessary that the mass of mixed double chlorides be freed from osmium as completely as possible. This may be done in the usual manner by repeated evaporation with nitro-hydrochloric acid.

PALLADIUM.

Test for the Presence of Palladium.

Carey Lea proposes hyposulphite of sodium as a delicate test for many of the platinum metals. For detecting the presence of palladium he proceeds as follows:—Place a solution of hyposulphite of sodium in a test-tube with a little liquid ammonia, and add a drop of the palladium solution, so that it shall communicate a pale lemon colour only to the liquid. By boiling this rapidly darkens to a wine-brown shade, increasing in intensity until it finally appears black. Dilution, however, shows that this results from its intensity only; the diluted liquid is free from turbidity, and has a warm brown tint.

Separation of Palladium from Copper.

Saturate the solution containing these metals with sulphurous acid gas, and add a solution of sulphocyanide of potassium. This has no action on the palladium, whilst it completely precipitates the copper in the form of a white sub-sulphocyanide.

RHODIUM.

Separation of Rhodium from Platinum.

The usual method of approximately separating these metals is, to convert them into their potassium or ammonium double chlorides, and then to

carefully wash out the rhodium salt by small successive portions of cold water, or, better, of a moderately concentrated solution of chloride of potassium or ammonium. By re-crystallising the platinum and rhodium salts respectively, they may be obtained in a state of purity, since they are not isomorphous.

To obtain rhodium absolutely free from platinum, Dr. Wolcott Gibbs advises to convert the two metals into the ammonium double chlorides, separate the rhodium salt as completely as possible by washing with a solution of sal-ammoniac, and then evaporate the double chloride of rhodium and ammonium with a solution of ammonia. In this manner the rhodium is converted into the chloride of the ammonia-rhodium base, discovered by Claus, $5NH_3,Rh_2Cl_3$, while the platinum forms no well-defined or crystallisable compound. The chloride of Claus's base may then be purified by repeated crystallisation.

IRIDIUM.

Separation of Iridium from Platinum.

The following process for separating these metals was proposed by Dr. Wolcott Gibbs:—The iridium is, in the first place, to be brought into the form of bichloride, by means of a current of chlorine or by nitric acid, and the two metals are then to be precipitated together as potassium double chlorides, by the addition of a concentrated solution of chloride of potassium. The colour of the mixed salts varies from orange to almost black, according to the quantity of iridium present. The mass of crystals is to be rubbed fine in an unglazed porcelain mortar, and boiling water added in the proportion of three volumes of water to one of salt. A dilute solution of nitrite of potassium is then to be added until the liquid becomes deep olive-green, carbonate of sodium being thrown in from time to time in quantity sufficient to prevent the solution from becoming strongly acid. The iridium is instantly reduced to sesquichloride, while the platinum salt remains as a reddish orange powder. The deep olive-green solution is to be poured off, and the undissolved mass treated a second time with hot water and nitrite. This process must be repeated as long as the liquid remains olive-green. The mixed solutions on cooling, or after evaporation, deposit a beautiful mass of crystals of the double chloride of potassium and sesquichloride of iridium. By re-solution and repeated crystallisation, the iridium salt may be obtained perfectly free from platinum. The undissolved mass and the mother-liquors from the iridium salt contain a large quantity of platinum with a comparatively small quantity of iridium. When the absolute quantity of platinum salt is not very large, it may be dissolved in boiling water, a small quantity of alkaline nitrite added, and the solution

allowed to crystallise; the resulting chloroplatinate of potassium contains only a trace of iridium.

This process gives satisfactory results when carefully executed, but requires attention to two points. In the first place the alkaline nitrite must be added in quantity just sufficient to reduce the iridium from bichloride to sesquichloride, but not so as to produce further chemical changes by the formation of the double nitrite of iridium and potassium or sodium; with a very little experience this is easily managed. In consequence of the facility with which the double nitrite of iridium and sodium is decomposed by boiling with hydrochloric acid into the double chloride, $IrCl_2,NaCl$, it is better to use nitrite of sodium in the above process, because, in case an excess of nitrite is used, the mixed solution of double chloride and double nitrite can easily be brought to the form of the double chloride, $Ir_2Cl_3,3NaCl$, by boiling with hydrochloric acid, neutralising with carbonate of sodium, and then reducing the iridium to sesquichloride by cautiously adding a very dilute solution of nitrite of sodium.

In the second place, it may happen, as in working with crude platinum solutions obtained not from osm-iridium but from platinum ores, that the quantity of platinum is very large when compared with that of iridium. The process applies equally well to this case as far as the iridium is concerned, but it is difficult and troublesome to re-crystallise large quantities of a salt so insoluble as platino-chloride of potassium, and small quantities of the corresponding iridium salt are difficult to remove.

The following process can be recommended for giving chemically pure iridium when platinum is the only other metal present:—The greater portion of the platinum is first to be separated in the manner above pointed out. The solution of double chloride of iridium and sodium, $Ir_2Cl_3,3NaCl$, is then to be filtered, an excess of nitrite of sodium added, and the solution boiled until it assumes a clear orange-yellow colour. To the boiling solution sulphide of sodium is added drop by drop as long as this produces a cloudiness, and until a small quantity of the precipitated sulphide of platinum is re-dissolved. Dilute hydrochloric acid is then to be added cautiously until the liquid, previously allowed to become cold, is distinctly though faintly acid, when it is to be filtered and the sulphide of platinum in the filter washed continuously with hot water. The filtrate is then to be boiled with hydrochloric acid in excess, and the resulting iridiochloride of sodium evaporated, precipitated by a cold and strong solution of sal-ammoniac, and washed with the same. This salt, on ignition, yields pure iridium if the operation has been well conducted. It is, however, in all cases well, after separating the sulphide of platinum by filtration, to

neutralise the filtrate with carbonate of sodium, boil a second time with a little additional nitrite of sodium, and then add sulphide of sodium and proceed as before. In this manner every trace of platinum is removed, and the resulting iridium salt is chemically pure.

Separation of Iridium from Rhodium.

Iridium may be approximately separated from rhodium by the process recommended by Claus, which consists in taking advantage of the solubility of the double chloride of rhodium and ammonium, $Rh_2Cl_3,3NH_4Cl$, in moderately strong solutions of chloride of ammonium, in which the iridiochloride of ammonium is nearly insoluble. This method is difficult of application when the quantity of rhodium is small, and is at best tedious and unsatisfactory. A better method is the following:—To the solution containing the two metals, nitrite of sodium is to be added in excess, together with a sufficient quantity of carbonate of sodium to keep the liquid neutral or alkaline; the whole is then to be boiled until the solution assumes a clear orange-yellow or orange colour. If a green tint should be perceptible, more nitrite of sodium must be added and the solution again boiled. Both iridium and rhodium are converted into soluble double nitrites. A solution of sulphide of sodium is then to be added in slight excess, the liquid rendered slightly acid, filtered, and the dark brown sulphide of rhodium thoroughly washed. The filtrate is perfectly free from rhodium. This is boiled with excess of hydrochloric acid, evaporated, precipitated with sal-ammoniac, and treated as described in the method of preparing pure iridium given above. The sulphide of rhodium, together with the filter, is to be treated with strong hydrochloric acid, and sal-ammoniac added in quantity sufficient to form rhodiochloride of ammonium. Nitric acid is to be added from time to time in small quantities, until, with the aid of heat, the whole of the sulphide of rhodium is oxidised and dissolved. The liquid is then to be filtered, the filter well washed, and the filtrate and washings evaporated to dryness on a water-bath, when, after washing out the soluble salts with a strong solution of sal-ammoniac, the double chloride of rhodium and ammonium, Rh_2Cl_3,NH_4Cl, is left behind. This is insoluble in a cold saturated solution of sal-ammoniac, in which it may be washed once or twice to remove alkaline salts and any traces of iridium which may be present as sulphate. The rhodium salt is then to be purified by crystallisation, or converted into the chloride of Claus's rhodium-ammonium base by evaporation on a water-bath with a solution of ammonia. Sulphate of iridium does not give a basic compound under these circumstances. The chloride, $5NH_3,Rh_2Cl_3$, is then to be further purified by crystallisation.

OSMIUM.

Reduction of Osmic Acid.

A solution of osmic acid on addition of nitrite of potassium is reduced to osmious acid, which unites with the alkali, forming the well-known beautiful red salt. The solution may be evaporated to dryness without decomposition. The nitrite may, therefore, be added with great advantage when solutions containing free osmic acid are to be evaporated, or even transferred from one vessel to another. No other reducing agent answers the same purpose, as the osmium is obtained at once in a very convenient form for preservation. When a solution of osmic acid, to which nitrite of potassium has been added, is evaporated sufficiently and then allowed to cool, beautiful garnet-red octahedral crystals of osmite of potassium separate.

These should be dried over sulphuric acid, and not in contact with paper or organic matter, which partly reduces the osmious acid to the brown sesquioxide of osmium. Nitrite of potassium exerts no sensible action when boiled with a solution of osmiochloride of potassium; any salt which may be formed is very soluble in water.

Separation of Osmium from Iridium (Analysis of Osm-Iridium).

Wöhler's Method of resolving osm-iridium, consists in passing moist chlorine over the ore mixed with common salt and heated to low redness in a glass or porcelain tube. This method is invaluable in analysis, and gives excellent results in working the ore upon a small scale. In all cases, however, several repetitions of the process are necessary for complete resolution or reduction to a soluble form. On the other hand, it can scarcely be doubted that this method could be advantageously employed upon the large scale, if vessels of porcelain of large size and of a proper shape could be obtained. Such vessels might be constructed in the form of long and flattened ellipsoids, furnished at each extremity with wide tubes several inches in length, and would be of great utility in various chemical processes, No process of fusion with oxidising agents compares with Wöhler's method in point of elegance, as no iron or other impurities afterward to be removed are introduced by the process itself.

Fritzsche and Struve's Process is to treat the ore with a mixture of equal parts of hydrate and chlorate of potassium, by which a more or less complete oxidation is effected, without any sensible evolution of osmic acid. The temperature required in this process is not high, but large vessels must be employed, as the mixture froths very much at first. This process does not appear to possess any sensible advantage over that of Claus,

which is, moreover, less expensive, and can be carried out with smaller vessels.

Claus's Method of resolving the ore consists in fusing for an hour, at a red heat, a mixture of one part of ore with one part of caustic potash and two of saltpetre. The fused mass is to be poured out upon a stone, allowed to cool, broken into small pieces or powdered, and then introduced into a flask, which is to be filled with cold water and allowed to stand for twenty-four hours. The clear deep orange-red solution of osmiate and rutheniate of potassium is then to be drawn off by means of a syphon, and the black mass remaining again washed in the same manner. The finely-divided oxidised portion of the insoluble matter may now be separated from the unattacked ore by diffusion in water and pouring off, after the subsidence of the heavier ore. The unattacked ore is then to be fused a second time with potash and saltpetre and treated as before. Claus asserts that he has been able in this manner to resolve the Siberian osm-iridium completely in two operations.

Dr. Wolcott Gibbs, to whom the chemistry of the platinum metals is so greatly indebted, recommends the following process for the analysis of osm-iridium:—The ore, which is usually very impure, is in the first place to be fused with three times its weight of dry carbonate of sodium. The fused mass after cooling is to be treated with hot water, to remove all the soluble portions, and then the lighter portions are to be separated by washing from the heavy unattacked ore. In this manner the greater part of the silica and other impurities present may be removed. A previous purification of this kind is not indispensable, and may be omitted altogether when the ore is in plates or large grains, but it is very desirable when the ore is in fine powder, and greatly facilitates the subsequent action of the oxidising mixture. By cutting off the top of a mercury bottle a wrought-iron crucible is obtained, in which 600 grms. of osm-iridium may be fused at one operation with potash and saltpetre as above. There is usually little or no foaming, and if any occur it may easily be checked by stirring with an iron rod. No sensible quantity of osmic acid is given off during the process, which with a little care is entirely free from danger. In this manner 1500 grms. of ore have been worked up in a few hours in three successive operations. The fused mass is to be broken into pieces with a hammer, and brought into a clean iron pot. Boiling water, containing about one-tenth of its volume of strong alcohol, is then to be added, and the whole is to be boiled over an open fire until the fused mass is completely disintegrated. The osmiate of potassium is, in this manner, reduced to osmite, while the rutheniate of potassium is completely decomposed, the ruthenium being precipitated as a black powder. It is advantageous, after boiling for some time, to pour off the supernatant liquid

with the lighter portions of the oxides, and boil a second time with a fresh mixture of alcohol and water. In this manner we obtain a solution of osmite of potassium, a large quantity of black oxides, and a heavy black and coarse powder. This last consists chiefly of undecomposed ore, mixed with a small quantity of the oxides of iridium, &c., with scales of oxide of iron from the crucible, and, if the ore has not been previously purified, with the impurities of the ore itself. The greater specific gravity of this residual mass renders it very easy to pour off from it the mixture of black oxides with the solution of osmite of potassium and alkaline salts. This solution with the suspended powder is to be poured into a beaker and allowed to settle. The heavy black powder remaining in the iron pot is then to be perfectly dried over the fire, and fused a second time with potash and saltpetre as before. The fused mass is to be treated exactly as after the first fusion. The heavy portions remaining after this operation may be fused a third time with the oxidising mixture. When, however, the ore has been previously purified by fusion with carbonate of sodium, or when it was originally in the form of clean scales, the heavy portion remaining after two successive oxidations will be found to consist chiefly of scales of oxide of iron.

The solutions containing osmite of potassium and alkaline salts are to be carefully drawn off by a syphon from the black oxides which have settled to the bottom of the containing vessels. The oxides may then be washed with hot water containing a little alcohol, and introduced into a capacious retort. By this process, when carefully executed, no trace of osmic acid escapes—an advantage not to be despised, as the deleterious effects of this body upon the lungs have not been exaggerated, and too much care cannot be taken to avoid inhaling it.

The solution of alkaline salts contains only a portion of the osmium in the ore. The other portion exists in the mixture of oxide, and must be separated by distillation. For this purpose the retort should be provided with a safety-tube, passing through the tubulure, and with a receiver kept cold, and connected by a wide bent tube with a series of two or three two-necked bottles containing a strong solution of caustic potash with a little alcohol, and also kept cold. All the tubulures and connections must be made perfectly tight. Strong hydrochloric acid is then to be cautiously poured into the retort, through the safety-tube, in small portions at a time. The reaction which ensues is often violent; great heat is evolved, and a portion of the osmic acid distils over immediately, and condenses in the receiver in the form of colourless needles. When a large excess of acid has been added, the action has entirely ceased, and the retort has become cold, heat may be applied by means of a sand-bath. The osmic acid gradually distils over, and condenses in the receiver and in the two-necked

bottles. Especial care must be taken that the beak of the retort is not too small at the extremity, as it may otherwise become completely stopped up with the condensed osmic acid. The same applies to the tubes connecting the receivers and two-necked bottles. The distillation should be continued for some time after osmic acid ceases to appear in the neck of the retort; when this has once become hot, the acid condenses, and passes into the receiver in the form of oily drops.

When the distillation is finished, the retort is to be allowed to cool, and then separated from the receiver, which is to be immediately closed with a cork. By gently heating the receiver in a water-bath, the contained osmic acid may be driven over into the two-necked bottles, where it condenses in the alkaline solution, and is reduced by the alcohol to osmite of potassium. The solution thus obtained may be added to that obtained directly from the fused mass of ore, and on evaporation in a water-bath and cooling, will yield crystals of osmite of potassium, the salt being but slightly soluble in strong saline solutions. The mother liquor from the crystals contain only traces of osmium, and may be thrown away as worthless.

The dissolved portions drawn off from the retort have a very dark brown-red colour. The solution is to be evaporated to dryness, re-dissolved in hot water and again evaporated, after adding a little hydrochloric acid, and this process repeated till no smell of osmic acid can be perceived. A cold and saturated solution of chloride of potassium is then to be added in large excess. This dissolves the chlorides of iron and palladium which may be present, leaving platinum, iridium, rhodium, and ruthenium as double chlorides, insoluble in a strong solution of the alkaline chloride.

The undissolved mass is to be well washed with a saturated solution of chloride of potassium, which is preferable to sal-ammoniac. In this manner nearly the whole of the iron and palladium may be removed, while any insoluble impurities contained in the ore remain with the mixed double chlorides.

For the separation of osmium from the other metals of the group, the best plan seems to be the one which is universally employed, namely, the volatilisation of the osmium in the form of osmic acid.

RUTHENIUM.

Preparation of Ruthenium from Osmide of Iridium (Osm-Iridium).

Osm-iridium almost always contains ruthenium, the amount of the latter metal increasing as that of the iridium decreases. The following process is the one recommended by Dr. Claus, the discoverer of ruthenium, for preparing this metal.

Osm-iridium is melted in the ordinary way with nitre and caustic potash,

and moistened with water; then nearly neutralise with sulphuric acid, in order to precipitate the metallic acids in solution, always leaving the liquid with a slight alkaline reaction; add alcohol and boil. Throw the mixture on a filter, and carefully wash in order to free it as far as possible from potassium salts. The black metallic powder thus obtained still contains sufficient potassium in the state of acid iridiate of potassium to convert the greater portion of the iridium into double iridic chloride during the subsequent solution of the metallic powder. For this reason evaporate to a considerable extent the aqua regia solution separated from the powder until all the osmium is disengaged as osmic acid; then, if left to cool, most of the iridium is deposited in the state of iridiochloride of potassium, and the liquid contains all the ruthenium in a much greater degree of concentration, although always associated with some iridium.

Afterwards filter and add powdered sal-ammoniac, which causes the deposition of yet more iridium as a black crystalline precipitate. The solution generally contains ruthenium so concentrated as to be separable from the iridium by precipitation. Now evaporate again and add more sal-ammoniac until the liquid begins to lose its colour, and most of the platinum metals are deposited as double salts. Then leave it for several days, collect the residue on a filter and wash it with water containing sal-ammoniac in solution, which completely eliminates iron and copper and does not affect the ruthenium. In this way there is obtained a residue of salts of iridium containing ruthenium, which, dissolved and boiled with the addition of a little ammonia, yields a precipitate of sesquioxide of ruthenium.

Commenting on the above process, Dr. Gibbs says that this method of treating the fused mass to separate ruthenium and osmium is liable to two sources of inconvenience. In the first place, the quantity of water required to dissolve out the soluble portions is very large, and the subsequent treatment of such bulky solutions by distillation with acids, tedious—very large retorts being necessary. In the next place, it is impossible in this way to avoid exposure to the vapour of osmic acid, especially in transferring the solutions from one vessel to another. He therefore recommends in preference the process which we have given at p. 294.

Estimation of Ruthenium.

When it is necessary to estimate ruthenium precisely, the osmium must not be expelled previously by means of aqua regia, otherwise there would be some loss of ruthenium. For the determination of ruthenium, a larger quantity of the alloy than is generally used is required,—that is to say, at least 10 grms., which must all be reserved for the search for ruthenium, disregarding all the other constituents. Melt the pulverised ore with

potash and saltpetre, dissolve it in water, carefully neutralise it with an acid, and, adding some alcohol, heat it; then carefully wash the precipitate, which is a black metallic powder, in water, to eliminate the saltpetre and other potassium salts. Dissolve this powder in hydrochloric acid, heat it in a retort with chlorate of potassium and hydrochloric acid, and collect the volatile products in condensers containing alcohol. By this means ruthenium and osmium are obtained together, but their separation can be effected by alcohol, which instantly decomposes the ruthenic acid, though it takes some time to reduce the osmic acid; or, the two metals may be precipitated from their solution by sulphuretted hydrogen, and the sulphides thus obtained heated in a small platinum vessel, in an oxygen current, which disengages sulphur and osmium as acids, while the ruthenium remains as ruthenic oxide.

There is no appreciable loss in melting ruthenium with caustic potash and saltpetre. A piece of paper soaked with alcohol does not blacken if held even for a long time over the heated mixture, and no smell of ruthenic acid is observable, though during the solution of the mixture a feeble odour of it is always given off. If ruthenious sesquioxide, which is obtained in treating this solution by alcohol, is dissolved in hydrochloric acid, the solution takes place without forming a volatile ruthenic combination; but there is some likelihood of loss if aqua regia is used as a solvent, for ruthenium is then placed under circumstances similar to those produced by the simultaneous action of chlorate of potassium and hydrochloric acid.

Detection of Ruthenium in the Presence of Iridium, &c.

The reactions of ruthenium are remarkably affected by the presence of iridium; and in proportion as this last-named metal is present in larger quantity, the indications afforded by most of the tests hitherto proposed grow less and less decided, and some lose all efficacy. Mr. C. Lea has discovered in hyposulphite of sodium a very delicate test for ruthenium.

When a solution of hyposulphite of sodium is mixed with ammonia, and a few drops of solution of sesquichloride of ruthenium are added, and the whole boiled, a magnificent red-purple liquid is produced, which, unless the solutions are very dilute, is black by transmitted light. The colouration is permanent, and the liquid may be exposed to the air without alteration. This reaction is obtained with great ease and certainty, and, in the opinion of the discoverer, is far superior to any known test for ruthenium. In order to determine the limits of the sensibility of this reagent, experiments were made with ruthenium solutions of different strengths. The following results were obtained:—

With 1-5000th of sesquichloride of ruthenium, bright rose-purple.

With 1-20,000th and 1-30,000th, fine rose colour.

With 1-50,000th, paler, but still perfectly distinct.

With 1-100,000th, the colour, though very pale, was still unmistakably present.

Where the solutions are so very dilute as these last, the boiling must be continued for some minutes.

When the presence of ruthenium in very small quantity, or in very dilute solution, is suspected, it is often advisable to boil the solution with a little hydrochloric acid, previous to the application of the hyposulphite test. The acidulated solution must be rendered alkaline by addition of ammonia before heating with hyposulphite.

This test is the best reagent that is capable of detecting ruthenium in the presence of any excess of iridium. No precautions are necessary, and the reaction is always obtained with the greatest facility. The iridium solution is to be rendered alkaline with ammonia, a crystal of hyposulphite of sodium is dropped into it, and the whole is boiled for two or three minutes. If no indication of a red-purple tint appears (or, in case of small quantites of ruthenium, a rose-colour), the iridium solution may be pronounced free from ruthenium.

Dr. Wolcott Gibbs has discovered another delicate test for ruthenium, which likewise can be employed in the presence of other platinum metals. When a solution of nitrite of potassium is added in excess to sesquichloride of ruthenium, either free, or in combination with chloride of potassium or ammonium, a yellow or orange-yellow colour is produced, but no precipitate is formed. A precisely similar change occurs when the ruthenium is in the form of bichloride; but in this case the change of colour is produced more slowly, and usually requires heating, or even boiling. The change of colour is due in both cases to the formation of an orange-yellow double salt of ruthenium and potassium, which is very soluble in water and alcohol; its relations to alcohol in particular enable us to distinguish ruthenium from the other platinum metals more perfectly than has hitherto been possible. When a few drops of sulphide of ammonium are added to a solution of this double salt a magnificent crimson colour is produced. This reaction furnishes a characteristic test of the greatest value, since it is not materially affected by the presence of the other metals of the same group.

The test may be most advantageously applied as follows:—The liquid supposed to contain ruthenium is first to be rendered alkaline by the addition of carbonate of sodium or potassium. Nitrite of potassium in solution is then to be added, the liquid boiled for an instant, allowed to become perfectly cold, and a drop or two of colourless sulphide of ammonium added. On shaking, the colour appears, and rapidly deepens to the finest red. When the quantity of ruthenium present is very small, or when large

quantities of the other platinum metals are also present, it is better, after adding the alkaline carbonate and nitrite, to evaporate the whole to perfect dryness on a water-bath, and treat the dry and powdered mass with a small quantity of absolute alcohol. The alcoholic solution is then to be filtered off, and tested directly with sulphide of ammonium. In this way the smallest trace of ruthenium may be detected even in the presence of very large quantities of the other platinum metals.

Dr. Claus detects ruthenium qualitatively in the presence of iridium by making use of the following reactions:—A solution of pure iridium, containing no ruthenium, is instantaneously decolourised by the addition of excess of caustic potash or ammonia. It remains thus for a long time perfectly transparent, and then, after several days, takes a beautiful blue colour. But if the iridium contains traces of ruthenium, the colour of the solution becomes fainter during the reaction, but does not disappear; it passes to a yellow-brown or reddish hue, and does not become decolourised for some time, at which point the solution becomes turbid, and a slight brown or yellow precipitate is formed. If the iridium contains more ruthenium, yet not sufficient to produce a visible precipitate, its presence is betrayed by the intense red-purple colour assumed by the liquid, especially if potash is used.

Separation of Ruthenium from Iridium.

The quantitative separation of ruthenium from iridium is much more difficult than the mere detection of ruthenium in the presence of iridium. Their separation cannot be effected by igniting them with a mixture of saltpetre and caustic potash. The following is an accurate means of separating the two metals, based upon Dr. Gibbs's discovery of the reaction of alkaline nitrites on ruthenium salts, described above:—

To the solution containing the two metals, nitrite of sodium is to be added in excess, together with sufficient carbonate of sodium to keep the liquid neutral or alkaline. The whole is to be boiled until the solution assumes a clear orange-yellow, or orange colour. If a green tint should be perceptible, more nitrite of sodium must be added, and the solution again boiled. Both ruthenium and iridium are converted into soluble double nitrites. A solution of sulphide of sodium is then to be added, in small quantities at a time, until a little of the precipitated sulphide of ruthenium is dissolved in the excess of alkaline sulphide. The first addition of the sulphide gives the characteristic crimson tint due to the presence of ruthenium, but this quickly disappears and gives place to a bright chocolate-coloured precipitate. The solution is then boiled for a few minutes, allowed to become perfectly cold, and then dilute hydrochloric acid added cautiously until the dissolved sulphide of ruthenium is precipitated and the reaction is just

perceptibly acid. The solution is then to be filtered through a double filter, and the sulphide of ruthenium washed continuously and thoroughly with boiling water. The filtrate is perfectly free from ruthenium; it is to be evaporated with hydrochloric acid, and treated with sal-ammoniac in the manner already pointed out in speaking of the separation of iridium from platinum (p. 291). The washed sulphide of ruthenium is to be treated, together with the filter, with strong hydrochloric acid, and chloride of ammonium added in sufficient quantity to form rutheniochloride of ammonium. Nitric acid is to be added from time to time, in small quantities, until, with the aid of heat, the whole of the sulphide of ruthenium is oxidised and dissolved. The liquid is then to be filtered, the filter well washed, and the filtrate and washings evaporated to dryness on a water-bath, when, after washing out the soluble salt with strong solution of chloride of ammonium, the rutheniochloride of ammonium remains almost chemically pure. It is to be dissolved and converted into the compound of chloride of mercury and ruthendiamin (see Separation of Ruthenium from Platinum). From this salt chemically pure ruthenium may be obtained by ignition, which is best effected in an atmosphere of hydrogen, as the reduced metal is easily oxidised in the air.

It may happen that the precipitated sulphide of ruthenium contains traces of iridium. This can only arise from imperfect washing or want of proper care in precipitating with sulphide of sodium. In this case, the washings from the rutheniochloride of ammonium are yellow, and contain sulphate of iridium. The quantity of iridium in such cases is too small to be worth the trouble of separate treatment.

When a solution contains iridium and ruthenium in the form of bichlorides, the ruthenium may be easily and completely separated by boiling the solution with nitrite of potassium in excess, adding, at the same time, enough carbonate of potassium to give an alkaline reaction, evaporating to dryness, and dissolving out the double nitrite of ruthenium and potassium by means of absolute alcohol. The undissolved mass in this case contains two double nitrites of iridium and potassium. By adding a strong solution of chloride of ammonium, evaporating to dryness, igniting the dry mass in a porcelain crucible, and dissolving out the soluble salts, metallic iridium remains in a state of purity. This method may be used for quantitative separation of iridium from ruthenium; but when the object is simply to prepare both metals in a state of chemical purity, the separation by means of sulphide of sodium is preferable.

Separation of Ruthenium from Rhodium.

The separation of rhodium from ruthenium is best effected by means of nitrite of potassium. The mixed solution of the two metals is to be boiled

for a short time with an excess of the nitrite, together with a little carbonate of potassium to keep the solution neutral or slightly alkaline. The yellow or orange-yellow solution is then to be evaporated to dryness upon a water-bath, the dry mass rubbed to fine powder and then treated in a flask with absolute alcohol in the manner pointed out for the separation of ruthenium from platinum. After filtration and washing with absolute alcohol, the rhodium remains undissolved in the form of a mixture of the two double nitrites of rhodium and potassium. These may be ignited with a large excess of sal-ammoniac, so as to yield, after washing, metallic rhodium; or the nitrites may be dissolved in hot hydrochloric acid, ammonia added, and the rhodium precipitated as sulphide, which is then treated in the manner already pointed out (p. 292), so as to convert the rhodium into the double chloride of rhodium and ammonium. To remove the last traces of ruthenium the rhodium salt may be a second time treated with nitrite of potassium, as above, and again washed with alcohol. The presence of the least trace of ruthenium is easily detected by adding a drop of colourless sulphide of ammonium to the alcoholic solution. The method of obtaining pure ruthenium from the double nitrite of ruthenium and potassium has already been given.

Separation of Ruthenium from Platinum.

The approximate separation of ruthenium from platinum may be effected by precipitating the two metals with chloride of potassium, and washing out the rutheniochloride of potassium with cold water, in which it is readily soluble. The mixed solutions should be evaporated to dryness with an excess of the alkaline chloride, and the dry mass rubbed to a fine powder in a mortar, after which almost the whole of the ruthenium may be washed out with water, or with a cold and moderately strong solution of chloride of potassium. The undissolved platinum salt may then be purified by crystallisation, but it usually contains traces of ruthenium. The rose-red solution of the ruthenium salt contains a small quantity of platinum, from which it cannot be wholly freed by the difference in solubility of the two salts. Chloride of ammonium may be employed in this process in place of chloride of potassium.

To obtain a complete separation, Dr. W. Gibbs's process may be followed with advantage:—The rutheniochloride of potassium, separated as far as possible from the platinum salt, is to be heated with a solution of nitrite of potassium in quantity sufficient to convert the whole of the ruthenium into the soluble yellow double nitrite of ruthenium and potassium, carbonate of potassium being added in small quantities so as to keep the solution neutral or alkaline. The yellow or orange solution is to be evaporated to dryness in a water-bath, the dry mass reduced to powder and boiled with absolute

alcohol until the ruthenium salt is completely dissolved. This is best effected in a flask furnished with a condensing-tube bent upwards, so that the alcohol vapours may be condensed and flow back into the flask. The boiling need not be continued for a very long time, as the ruthenium salt is readily soluble in alcohol. The solution is then to be filtered off from the undissolved salts, and these are to be washed with absolute alcohol until the washings are colourless, or until they no longer give the characteristic ruthenium reaction with sulphide of ammonium. The filtrate and washings may then be distilled, to separate and save the alcohol, water being added in small quantity. The residue in the retort or flask is then to be evaporated with hydrochloric acid, which readily decomposes the double nitrite, and yields a fine deep rose-red solution of the rutheniochloride of potassium, containing at most only a trace of platinum. The mass of salts undissolved by the alcohol contains nearly all the platinum in the form of platinochloride of potassium, which is easily separated. The solution of the rutheniochloride of potassium is now so pure that it gives the reactions of a chemically pure salt.

To obtain the ruthenium in a state of absolute purity, the solution is to be evaporated to dryness with a saturated solution of sal-ammoniac in excess, re-dissolved, again evaporated, and the dry mass washed with a little cold water to remove the alkaline chlorides. The rutheniochloride of potassium is in this manner, for the most part at least, converted into the corresponding ammonium salt. This salt is then to be dissolved in hot water, a solution of ammonia added, and the liquid boiled until it assumes a clear yellow or orange-yellow colour, after which it is to be evaporated to dryness on a water-bath. In this manner the ruthenium is converted into chloride of ruthen-diamin, discovered by Claus. The yellow mass is to be dissolved in boiling water, and a solution of chloride of mercury added. A beautiful yellow crystalline double salt is precipitated, and the mother-liquor, when cold, contains only traces of ruthenium and platinum. The double chloride of mercury and ruthen-diamin is almost insoluble in cold water, but is soluble in boiling water, and is easily rendered absolutely pure by re-crystallisation. On ignition, this salt yields chemically pure metallic ruthenium as a silver-white porous mass.

When, in a mixture of solutions of ruthenium and platinum, the ruthenium is present either partly or wholly as sesquichloride, the liquid is to be boiled with nitrite and carbonate of potassium as above, evaporated to dryness, boiled with excess of hydrochloric acid to convert the double nitrite of ruthenium and potassium into rutheniochloride of potassium, and the resulting solution treated by the process already described.

CHAPTER XI.

SULPHUR, PHOSPHORUS, NITROGEN.

SULPHUR.

Estimation of Sulphur in Pyrites.

A. *Estimation of Sulphur in the Dry Way.*—Fuse the weighed ore with a weighed quantity of anhydrous carbonate of sodium, twice as much chlorate of potassium as ore, and from 12 to 20 times as much chloride of sodium (added to moderate the action); carbonic acid is expelled, chloride of potassium formed, and all the sulphur converted into sulphate of sodium; by dissolving the residue in water and estimating alkalimetrically the unaltered carbonate of sodium by a standard acid solution, the portion converted into sulphate, and hence the sulphur in the ore, is known. Besides the difficulty of preventing loss by deflagration, this method is open to the small errors caused by the reckoning all arsenic present to be sulphur: this, however, is usually of no moment for commercial purposes; any carbonate of calcium in the ore may, if required, be previously dissolved out by dilute hydrochloric acid.

In performing fusions of sulphur compounds with nitre or chlorate of potassium, the operator must bear in mind a source of error, first pointed out by Dr. David S. Price, in consequence of sulphur compounds being contained in the coal-gas which frequently serves as fuel in these experiments. By exposing a small quantity of melted nitre, on the *outside* of a platinum capsule, to the flame of a Bunsen gas-burner for three quarters of an hour, Dr. Price succeeded in detecting the presence of sulphuric acid to an amount equivalent to 12 milligrammes of sulphur. This sulphate had been formed by the oxidation of the sulphur in the coal-gas, and, when dissolved in water, gave an immediate precipitate with chloride of barium. By making a similar experiment with the use of a spirit lamp as the source of heat, no trace of sulphate of potassium was formed; nor was any appreciable amount of sulphuric acid generated in another trial made by fusing a small quantity of nitre *inside* a platinum capsule heated over gas; but whenever the fused salt crept over the edges of the capsule, some of the sulphate was sure to be formed. This observation may become a matter

of importance when the amount of sulphur in pig-iron is determined by fusion with pure nitre, for the author has remarked that samples containing much manganese are especially liable to impart to the fused salt a tendency to creep up and escape over the sides of the crucible.

B. *Estimation of Sulphur in the Wet Way.*—Mr. C. R. A. Wright recommends the following process as being the one best adapted for commercial purposes:—A known weight of the ore reduced to fine powder is oxidised (best in a small flask with a funnel placed in the mouth to avoid loss by spirting, and heated on a sand-bath) either by strong nitric acid, or aqua regia, perfectly free from sulphuric acid; after the oxidation is complete, the liquid is evaporated down as far as possible to expel the majority of the remaining nitric or hydrochloric acid; the residue is boiled with a little water, and almost but not quite neutralised by ammonia; a solution of chloride of barium of known strength is then added until no further precipitate is produced, the exact point being found by filtering off a little of the liquid after each addition of chloride of barium and adding to it a few more drops of the standard solution, care being always taken, in case of a further precipitate being thus produced, to add this filtrate to the original solution, and mix well before filtering a second time. In case of overstepping the mark, it is convenient to have at hand a solution of sulphate of sodium of strength precisely equal to that of the chloride of barium; this solution may then be cautiously added, with repeated filtration and examination of the filtrate with the sulphate solution, until the point is just reached, when addition of sulphate solution produces no further precipitate: by subtracting the volume of sulphate solution thus used from the total volume of barium solution added, the exact quantity of this latter consumed is known. If 1 grm. of sulphur ore be taken, and 32·5 grms. of pure anhydrous chloride of barium be dissolved to a litre of fluid, each cubic centimetre of barium solution used will represent ½ per cent of sulphur in the ore examined; 22·19 grms. of anhydrous sulphate of sodium being dissolved to a litre for the second solution. In case of lead being contained in the ore, an error is introduced from the formation of insoluble lead sulphate; as lead, however, rarely occurs in any perceptible quantity, this error is negligible, the process only giving approximate results.

Where greater accuracy is required, it is advisable to precipitate the sulphuric acid formed from the original liquid (filtered from insoluble residue) by chloride or nitrate of barium, and to weigh the sulphate of barium produced. Instead of oxidising by acids, the powdered ore may be suspended in caustic potash (free from sulphate), and oxidised by passing washed chlorine into the liquid; lead, being converted into dioxide, is thus rendered non-injurious; the alkaline liquid obtained is acidified, and precipitated by chloride of barium as before. In the volumetric determination

usually pursued, a curious circumstance is occasionally observable when much free acid exists in the solution, viz., that a point may be reached when the filtered liquid is clear, and remains so even on standing for a short time, but yields a cloud, or even a precipitate, on the addition either of barium solution or sulphate solution; this source of error is mostly avoidable by nearly neutralising the free acid with ammonia.

Instead of chlorine, hypochlorous acid may be used to transform the sulphur of pyrites into sulphuric acid, which is then estimated by barium. Finely pulverise the mineral and suspend it in water, through which a current of gaseous hypochlorous acid, or, better still, hypochloric acid, is passed; this entirely dissolves the pyrites. Hypochlorous acid is prepared by heating a milk of carbonate of calcium through which a current of chlorine is passed to saturation. Hypochloric acid is obtained by heating in a water-bath a tube, supplied with a cork and delivery tube, and containing a mixture of nine equivalents of oxalic acid and 1 equivalent of chlorate of potassium.

Mr. A. H. Pearson has given the following very accurate method of estimating sulphur in pyrites:—Weigh out 1 grm. or less of the powdered ore, place the powder in a porcelain dish, together with a small quantity of chlorate of potassium, pour upon it some 50 c.c. of pure nitric acid of 39° B., and cover the mixture with an inverted glass funnel with bent stem. Set the dish upon a water-bath, and heat the water to boiling. From time to time throw crystals of chlorate of potassium into the hot acid. By adding rather large crystals of the chlorate at frequent intervals, it is easy to oxidise the whole of the sulphide in half-an-hour; but, since the solution obtained in that case is highly charged with saline matter, it will usually be found more advantageous to use less of the chlorate of potassium, and to allow a somewhat longer time for the process of oxidation.

When all the sulphur has been oxidised, rinse the funnel with water, and remove it from the dish. Evaporate the liquid to a small bulk, then add to it a little concentrated hydrochloric acid, and again evaporate to absolute dryness, in order to render silicic acid insoluble. Moisten the residue with concentrated hydrochloric acid, mix it with water, and filter to separate silicic acid and gangue.

To the filtrate from the silicic acid add a quantity of solid tartaric acid, about as large as that of the pyrites originally taken; heat the liquid almost to boiling, and add to it an excess of chloride of barium, to precipitate the sulphuric acid. After the sulphate of barium has been allowed to subside, wash it thoroughly by decantation, first with hot water, and afterward with a dilute solution of acetate of ammonium (the latter may be prepared at the moment of use by mixing ammonia-water and acetic acid). The purpose of the acetate of ammonium is to dissolve any nitrate of barium which may adhere to the sulphate; that of the tartaric acid is to

prevent the precipitation of iron compounds together with the sulphate of barium. In an experiment where 0·7 grm. of pyrites was oxidised with chlorate of potassium and nitric acid, and the filtrate from silica was acidulated with hydrochloric acid without the addition of tartaric acid, there was thrown down, on the addition of chloride of barium, a bright yellow precipitate, which became darker-coloured when the solution was boiled. It was not only found to be impossible to wash out the iron with which this precipitate was contaminated, but the consistency of the precipitate was such that it was a difficult matter even to wash away the saline liquor in which it was formed.

In another experiment, the attempt was made to remove the iron from the filtrate from silica, before adding the barium-salt to throw down the sulphuric acid; but in that case a considerable portion of the sulphuric acid was dragged down as sulphate of potassium by the iron precipitate, and so lost. The precipitation of the iron was effected, in this experiment, by adding an excess of ammonia-water to the acidulated filtrate from silica, and washing the precipitate for a long time by decantation with boiling water. To prove that the iron precipitate really retained sulphuric acid, a quantity of the precipitate was dried, ignited, and powdered, and the powder boiled with water. The clear liquid thus obtained was acidulated with hydrochloric acid, and tested with chloride of barium. An abundant precipitate of sulphate of barium was at once thrown down.

Estimation of Sulphur in Iron, Steel, and Iron Ores.

This estimation has been fully treated of in the chapter on Iron. (See pp. 84 to 93.)

Estimation of Sulphur in Vermillion.

A mixture of nitric acid and chlorate of potassium is the best means of oxidising the sulphur in this mineral to sulphuric acid, as no trace of free sulphur is ever seen in the liquid, whilst when hydrochloric acid is used to decompose the chlorate, globules of sulphur float about and entirely resist solution. About 0·5 or 0·6 grm. of the vermillion is placed in a small glass flask, set in an inclined position upon a wire-gauze support above a lamp. A quantity of nitric acid of 39° B., is poured into the flask; a small quantity of chlorate of potassium then added, and the mixture heated. From time to time, crystals of chlorate of potassium are thrown into the flask, the contents of which are maintained near the boiling-point until all the sulphur has dissolved. It sometimes happens, when the proportion of nitric acid is small, that a considerable quantity of saline matter crystallises in the flask; enough water to re-dissolve this precipitate may, however, be added to the mixture, without impairing to any material extent the oxidising power of the chlorate subsequently added.

The acid liquor resulting from the action of nitric acid and chlorate of potassium upon the vermillion is evaporated to dryness on a water-bath, and the residue treated with strong hydrochloric acid, in order to destroy most of the nitric acid before proceeding to precipitate the sulphuric acid with chloride of barium. Before adding the hydrochloric acid to the residue, the latter must be allowed to become perfectly cold, lest the mixture froth violently, and portions of it be thrown out of the flask. After the acid has once been added, however, the mixture may be heated gently without risk of loss. The solution must at last be largely diluted with water before adding the chloride of barium.

Estimation of Sulphur in Mineral Waters.

Mr. F. Maxwell Lyte has devised an ingenious method of estimating free sulphuretted hydrogen in a mineral water when accompanied by proto-sulphate of iron, the presence of which interferes with the usual tests. Some sulphate of lead is prepared by precipitation from boiling solutions, and is well washed with boiling distilled water, and, while still fresh and moist, successive portions are added to the mineral water till the brownish-black colour of the precipitate first formed turns to a decided grey, showing that the sulphuretted hydrogen has all been removed from the solution and that some undecomposed lead salt remains in excess. The supernatant liquid is decanted from the precipitate, which rapidly settles down, and the latter is rapidly washed on a filter with boiling distilled water, and subsequently with hot solution of acetate of ammonium to dissolve out the excess of sulphate of lead, till the washings are no longer coloured by the addition of an alkaline sulphide. The filter is now carefully incinerated, and the sulphide of lead oxidised by an addition of a little nitric acid, and evaporated with a little sulphuric acid until heavy fumes of the latter begin to be evolved. Subsequent dilution with water gives a precipitate of sulphate of lead, which is separated by decantation and weighed; from this may be calculated the amount of sulphuretted hydrogen which has been present in the water.

Detection of Sulphur by means of Sodium or Magnesium.

Dr. Schönn recommends the use of either of these two metals for ascertaining the presence of sulphur in the oxidised or non-oxidised state in compounds. The substance to be tested (for instance, the sulphate of calcium or barium) thoroughly mixed, previously reduced to powder, and next heated to redness with the metal in a test-tube made of thin hard glass. After the reaction is over, the contents of the tube are, when quite cold, treated with distilled water and tested with nitro-prusside of sodium. Care should be taken that only small quantities of substance are operated

upon in this manner, especially as substances like realgar, orpiment, and others containing sulphur and arsenic, at the same time detonate violently when ignited with sodium.

As regards liquids containing sulphur, the author states that a drop of sulphuric acid, when brought into contact with sodium, yields, among the products of the reaction, sulphuret of sodium; with magnesium, this reaction does not take place unless heat be applied. Sulphide of carbon and essential oil of mustard may be readily proved to contain sulphur by application of the same test. For detecting sulphur in organic substances, especially of animal origin, the same process is available. Hair and feathers, and dry skin and nails, may be at once submitted to ignition with the metal. White of egg, emulsin, saliva, or muscle should first be calcined on a piece of platinum, and the animal charcoal so obtained be ignited along with sodium or magnesium. In most cases of this kind, nitro-prusside of sodium will be required to make the presence of sulphur distinctly evident.

Reagent for Sulphur.

According to Dr. Schlossberger, a solution of molybdate of ammonium in hydrochloric acid, diluted with water, possesses the property of becoming coloured blue, if traces of sulphur are present. By this means the presence of sulphur even in a single hair is easily recognisable after it is rendered soluble by the method just given.

Preservation of Sulphuretted Hydrogen Solution.

By adopting an artifice first proposed by Mr. Lepage, sulphuretted hydrogen solution can be kept for twelve or fifteen months with scarcely any loss of strength. Instead of using water, saturate a mixture of pure glycerine and water with sulphuretted hydrogen gas and use it in the ordinary manner. This liquid dissolves rather less sulphuretted hydrogen than distilled water does, but none of the reactions are interfered with in the least, whilst the solution possesses almost perfect stability. Glycerine likewise prevents solution of sulphide of ammonium from becoming coloured.

Anomalies in the Detection of Sulphuric Acid.

In testing for sulphuric acid in the presence of phosphoric acid, attention must be directed to a remarkable case of interference which appears to have escaped observation until it was pointed out by Mr. Spiller.

If to an aqueous solution of glacial phosphoric acid a small proportion of sulphuric acid be added, the mixed liquid does not give the usual indication of a precipitate on adding a few drops of chloride of barium, but requires a liberal addition of the last-named reagent in order to induce the formation

of the sulphate. By adding dilute hydrochloric acid, or by raising the temperature of the clear barytic solution, the formation of a precipitate is determined; but continued ebullition fails, in many instances, to separate the whole of the sulphate of barium. When, however, by the action of heat and of hydrochloric acid conjointly, the white precipitate makes its appearance, it is always found to be markedly different in physical character from the product usually obtained, being thrown down in the form of a semi-transparent flocculent precipitate, very like that obtained through the intervention of an alkaline citrate, as described in Mr. Spiller's paper, entitled "On the Influence of Citric Acid on Chemical Reactions,"* read before the Chemical Society.

This remarkable property of obscuring the indication of sulphuric acid appears to be possessed only by the glacial modification of phosphoric acid; for, if the white flakes of phosphoric anhydride (as obtained by the combustion of phosphorus) be dissolved in water, no such result is apparent; nor do the hydrochloric acid solutions of bone-ash and of the ordinary phosphate of sodium mask, in any appreciable degree, the presence of sulphuric acid. But if by heat the ordinary crystals of phosphate of sodium be converted into pyro-phosphate, and then dissolved in dilute hydrochloric acid, a solution is obtained which in this particular exactly resembles the glacial modification of phosphoric acid.

Detection of Free Sulphuric Acid in Vinegar.

Boil about 50 c.c. of the acid to be tested in a retort with a very small quantity of starch, until half the liquid is distilled; after it has cooled add a drop of tincture of iodine. If, under these circumstances, a blue colouration be produced, no sulphuric acid is present. If the blue colour does not appear, it may be concluded that sulphuric acid is present, which, by reacting on the starch, will have transformed it into glucose. With tincture of iodine, glucose gives no particular colouration.

Volumetric Estimation of Sulphuric Acid.

Prepare a standard solution of nitrate of lead containing 33·100 grms. in each litre. This lead solution is added to the fluid containing the sulphuric acid in such proportion as to allow a slight excess of lead, after which the precipitate is filtered and washed, and the filtrate mixed with acetate of sodium, and the excess of lead estimated by means of a standard solution of bichromate of potassium, according to the process described at pp. 212, 213. The lead precipitate is far preferable to the barium precipitate, as it subsides readily, filters clear, and is easily washed.

* See the "Chemical News," vol. viii., p. 280.

Every cubic centimetre of the above lead solution requires 0·008 grm. of sulphuric acid for precipitation.

Sulphate of lead is slightly decomposed by bichromate of potassium; it is therefore necessary to remove it by filtration, before the excess of lead can be estimated. The quick and complete deposition of this precipitate enables us, however, to remove, by means of a pipette, a certain portion of the clear fluid, and to estimate the amount of the lead it contains, and calculate the whole without any filtration at all. There is no doubt that most sulphates may be analysed in this way; ammonia-iron-alum, sulphate of copper, sulphate of magnesium, each give very accurate results when subjected to trial; acetate of iron alone, on account of its red colour, occasions some inconvenience in well observing the silver reaction.

Should, however, the base occasion some inconvenience, as, for instance, in sulphate of calcium, it may be removed by boiling with carbonate of sodium, and the sulphuric acid estimated as usual in the filtrate.

Hydrochloric acid is the most troublesome of the acids, as in concentrated solutions chloride of lead as well as sulphate, is precipitated; and as mixtures of sulphates and chlorides frequently occur, it is necessary to add to these nitric acid, to evaporate them to dryness, and to expel in this way every trace of chlorine. Weaker acids, such as hydrosulphuric acid, are thereby also expelled.

Another method, simpler, but not quite so accurate, for the volumetric estimation of sulphuric acid is the following:—The solution is coloured with litmus, and very carefully neutralised; a solution of chloride of barium of known strength is added in excess, and all the sulphuric acid thereby precipitated. Next, a titrated solution of carbonate of sodium is added, in order to precipitate the excess of barium; and then, again, the excess of sodium solution used is estimated, volumetrically, by means of titrated dilute sulphuric acid. During these operations, no salt is formed which can injure the colour of the litmus. In case salts are present in the original solution, the bases of which could be precipitated by carbonate of sodium, that precipitation is performed previous to the addition of soda. The filtrate, which contains the sulphuric acid combined with sodium, is neutralised, and again volumetrically titrated. The solutions required for this experiment are:—A solution of chloride of barium, containing 52 grms. to the litre of water; a solution of carbonate of sodium, containing 26·5 grms. of this salt to the litre of water; a solution of sulphuric acid, containing 20 grms. of monohydrated sulphuric acid to the litre of water. These solutions agree among each other, drop for drop. The advantage claimed for this method by its author, Dr. Clemm, is the non-necessity of having to wash out the sulphate and carbonate of barium, and also that titration does

not take place in a fluid rendered turbid by suspended sulphate of barium, which always tends to render the observation of colouration of litmus difficult.

Estimating Free Sulphuric Acid in Superphosphates.

The following method is recommended by Dr. R. Carter Moffat as being very accurate:—An aqueous solution of the superphosphate being made, evaporate slowly until a small quantity only is left; add about seven volumes of concentrated alcohol, and allow it to settle in the cold for some hours. This precipitates all sulphates, and leaves in solution, besides phosphates, the free sulphuric acid. Filter, wash with alcohol, add a large amount of water to the solution, carefully evaporate off the spirit, and estimate the acid in the usual manner by precipitation with chloride of barium. The soluble phosphates do not in any way interfere.

Should a more ready, though less accurate, process be required, an aqueous solution of the superphosphate treated with a very dilute normal solution of ammonia gives tolerably fair results.

Precautions in Precipitating Sulphate of Barium.

It is well known that precipitated sulphate of barium may retain alkaline salts in quantities of from 1·5 to 2 per cent, which cannot be removed by the most careful washing. Stolba obtains the sulphate of barium pure by digesting it (after washing until the wash-waters no longer react of barium) with 40 to 50 c.c. of a cold saturated solution of neutral acetate of copper and some acetic acid, at nearly a boiling heat for 10 or 15 minutes. During the digestion, enough acetic acid must be present to prevent the formation of basic salt on boiling. Should basic salt form, which may be readily perceived at the bottom of the vessel, more acetic acid must be added, and the digestion must be renewed for 10 or 15 minutes. During the process, the vessel containing the precipitate should be constantly agitated. The alkaline salts retained by the sulphate of barium undergo double decomposition with acetate of copper, and the resulting products all admit of entire separation from the precipitate by means of hot water. The precipitate is washed until no reaction for copper is manifested on testing the washings with ferrocyanide of potassium. This method is also satisfactory for the estimation of sulphuric acid in presence of a large excess of nitrate and chloride of barium.

The commercial crystallised acetate of copper is purified from sulphuric acid, and at the same time saturated with sulphate of barium, by adding to its boiling solution a slight excess of chloride of barium and acetic acid, and filtering from the precipitate.

Purification of Sulphuric Acid from Arsenic.

Arsenic almost always exists in commercial sulphuric acid in the form of arsenious acid, which, being volatile, distils over with the sulphuric acid, and prevents its purification by rectification. If, however, previous to distillation, the arsenious acid is oxidised to the form of arsenic acid which is non-volatile, the sulphuric acid which comes over on distillation will be quite free from arsenic.

MM. Bussy and Buignet recommend that a sulphuric acid which contains arsenious acid should be boiled with nitric acid, to oxidise arsenious acid to arsenic acid, then mixed with a little sulphate of ammonium to destroy the excess of nitrous compounds, and distilled with precautions to prevent any particles being carried over by projection. The distillate will be free from arsenic.

As there is some theoretical danger that the sulphate of ammonium might reduce the arsenic acid to arsenious, which would pass over as before, M. Blondlot recommends that peroxides of manganese should be used to oxidise the arsenious acid. The way he proceeds is as follows:—Peroxide of manganese is added in the proportion of 4 to 5 grms. to the kilogramme of sulphuric acid, and the mixture heated to boiling in a porcelain dish, stirring all the time. It is allowed to cool, and is then transferred to a retort and distilled.

Maxwell Lyte employs a different mode of purification, chiefly with a view to ensuring the complete absence of all nitrous products, and obtaining a pure acid from the very first, and of thereby obviating the necessity of changing the receiver,—a most dangerous operation when distilling sulphuric acid. If the acid contains nitrous compounds, heat it in a porcelain capsule to a temperature of about 110° C., with a small portion of oxalic acid, till the latter is completely decomposed, and all effervescence has ceased; about $\frac{1}{4}$ to $\frac{1}{8}$ per cent is amply sufficient for nearly all samples of commercial acid. It is best to add the oxalic acid before heating, and to stir constantly till the reaction is completed. Now allow the acid to cool down to about 100° C., and add to it a solution of bichromate of potassium in sulphuric acid, or some of the salt itself in fine powder, until the pure green colour at first produced by the formation of sesquioxide of chromium is replaced by a yellowish-green, indicating an admixture of chromic acid in the free state. The acid so prepared, being now distilled, passes from the first perfectly free from all impurity. The addition of the bichromate has another advantage, viz., that if it be first of all applied to a small sample of the commercial acid, it indicates the presence of free sulphurous acid, as well as of arsenious acid, and either of these being present, we may presume on the absence of nitrous compounds.

No doubt permanganates would answer equally well; but the bichromate of potassium, which is cheap and easily procured, is so convenient and inexpensive as to leave nothing to be desired.

Detection of Gaseous Impurities in Sulphuric Acid.

It is essential for some purposes that oil of vitriol should contain neither sulphurous acid nor any of the lower oxides of nitrogen; both of these impurities are met with in some commercial samples of oil of vitriol. Mr. R. Warington gives the following method for testing for the presence of sulphurous acid and oxides of nitrogen.

About two pounds of the oil of vitriol are placed in a bottle, which the liquid half fills; the bottle is then stoppered, and violently shaken for a minute or two. The gases contained in the oil of vitriol are thus washed out by the atmospheric air contained in the bottle. Sulphurous acid is then tested for by introducing into the air space of the bottle a slip of paper coloured blue by iodine and starch; the paper is conveniently held in the bottle by means of a wire and a cork. The bleaching of the paper gives evidence of the presence of sulphurous acid.

The test-paper is best prepared from Swedish filter paper; this is first passed through a well-made solution of starch, and then dried. A slip of this paper is next placed in a weak aqueous solution of iodine, where it remains till it has acquired a distinct blue colour. It is then removed, pressed between blotting-paper, and is now ready for use.

The paper thus prepared gradually loses its colour by exposure to air, it should therefore be used as soon as made; for the same reason its exposure to the gas in the bottle should not exceed two or three minutes; no perceptible change of colour will occur in this time if no sulphurous acid be present. The colour of the paper is also at once destroyed by heat; it cannot therefore be used for testing the gases given off by hot liquids.

The nitric oxides are detected by substituting for the first test-paper one imbued with iodide of potassium and starch. As NO forms NO_2 on contact with air, and N_2O_3 produces the same compound on contact with air and moisture, the presence of either of these three oxides will suffice to liberate iodine on the moist test-paper, and colour the starch. Since sulphurous acid destroys the blue iodide of starch, the presence of an excess of this gas will prevent the detection of the nitric oxide. The nitric oxide is, on the other hand, without effect on the test-paper employed for the sulphurous acid. If, therefore, the sulphurous acid is not in excess, it is quite possible to obtain the reactions of both gases from the same sample of oil of vitriol, and this is no uncommon occurrence with oil of vitriol which has been imperfectly boiled.

In using the reaction here described for the purposes of general testing, it is to be remembered that sulphuretted hydrogen produces the same effect as sulphurous acid.

Detection of Sulphurous and Hyposulphurous Acid.

Instead of employing hydrochloric acid and zinc, aluminium and hydrochloric acid are preferable. Zinc may be contaminated with sulphur compounds, while aluminium is always pure in this respect; the latter metal, moreover, dissolves very slowly in dilute hydrochloric acid, and, therefore, the same piece of aluminium may serve for many testings. Dr. Reichardt has distinctly detected the sulphuretted hydrogen when a solution of one part of sulphurous acid in water, diluted with 500,000 parts of water, was treated with hydrochloric acid and aluminium.

PHOSPHORUS.

Detection of Phosphorus.

When previously well dried (previous ignition is often required) inorganic combinations of phosphorus are ignited in a pulverised state in a test-tube with small quantities of magnesium wire, ribbon, or powder, there is formed phosphide of magnesium. After cooling, the fused mass, on being moistened with water, will disengage phosphuretted hydrogen gas, which, in many instances, will be found to be the spontaneously inflammable variety. Phosphorus may be detected in the same way in organic substances; as, for instance, brains, muscle, &c.; but these should be previously calcined, and the dry animal charcoal so obtained submitted to the experiment.

For the detection of phosphorus in organic liquids, the following modification of Mitscherlich's process will be found to answer well. In this process the presence of phosphorus is established by the phosphorescence imparted to the aqueous vapours on distilling the liquid or liquefied mixture, and the distillation of the phosphorus is increased by the addition of sulphuric acid, chloride of sodium, sugar, &c., whereby the boiling-point of the liquid is made to approach that of phosphorus.

In the place of Mitscherlich's apparatus, the following more simple one is proposed; it is easily prepared and readily taken apart. It consists of an ordinary flask, connected with a receiving-bottle by means of a glass tube, which passes about 18 inches through a glass cylinder filled with cold water. A long straight tube conducts the gaseous products from the bottle. The lamp and flask, and about three-fourths of the glass cylinder, are surrounded with dark paper. The operation is best performed in a dark room.

The phosphorescence of the liquid increases in intensity with the consistence of the liquid and the quantity of the phosphorus. The gas-bubbles are luminous, rise in the mixture, and apparently burn upon its surface with a bright flame. With the temperature the light increases; a photosphere fills the flask, rises in the tube, and moves up and down within the cooled part. Sometimes only a column or a luminous ring appears stationary at the point where the vapours are cooled, and a luminous fog or sparks gradually sink into the receiver, or a sudden, frequently-repeated lightning is observed. If the heat is raised too high, or the cooling is insufficient, the phosphorescence passes through the long gas-tube, at the mouth of which the gases take fire, if the volatile oils from *Cruciferæ* (mustard, &c.) have been present.

Coffee, mustard, smoked meat, highly-seasoned food and beverages, and medicines containing odorous gum-resins, volatile oils, musk, camphor, chlorine, &c., have the property of covering the odour of a small portion of phosphorus.

The reaction is not interfered with by the presence of ipecacuanha, tartar emetic, magnesia, hydrated oxide of iron, musk, castor, opium, albumen, neutral acid or basic salts and double salts, volatile organic acids, chlorides, iodides and sulphides, and free acids; but iodine, chloride and bichloride of mercury in considerable proportion, and metallic sulphides in the presence of free sulphuric acid, and particularly *oleum cinæ* (*Artimisiæ*), interfere with or prevent the reaction.

Numerous experiments, by distilling the brain of various animals, blood, albumen, casein, fibrin, legumin, and other protein compounds, with dilute sulphuric acid, have not yielded the least photospheric reaction.

Detection of Arsenic in Commercial Phosphorus.

In preparing dilute phosphoric acid by the oxidation of commercial phosphorus, the precaution should be taken to pass a current of sulphuretted hydrogen through the solution, in order to free it from all substances precipitable by that agent from acid solutions; by this operation sulphide of arsenic is frequently thrown down; in order to estimate the amount Dr. C. J. Rademaker oxidised 100 grms. of phosphorus with nitric acid, diluted the solution and precipitated the arsenic as sulphide, by means of sulphuretted hydrogen; the solution was allowed to rest for six days, after which the precipitate was collected on a filter and washed, transferred to a small evaporating dish, oxidised with nitric acid, reduced by means of sulphurous acid to arsenious acid, again precipitated by means of sulphuretted hydrogen; the precipitate digested with ammonia to free it from adhering sulphur, the solution filtered, evaporated, dried, and weighed, when it was found to amount to nearly 1 grm. of sulphide of arsenic.

Phosphorus Holder.—Mr. E. Kernan gives the following ingenious method of making a phosphorus crayon which is perfectly safe in the hand for lecture experiments in luminous writing, &c.:—A few inches of lead tube, ¼ in. bore, are contracted to an open cone, at one end. As much phosphorus as one may choose is put into the cone of the tube; the phosphorus is made to project slightly from the cone; the upper part of the tube is filled with water, and corked. To put in the phosphorus, as much as may be required is melted in a conical glass, or test-tube, the cone of which is larger than that of the lead tube. This is put standing in the melted phosphorus, which fills the cone and tube to its own outside level. When cold, there is a nice projecting crayon, from the form of the glass. Any phosphorus outside the lead tube may be melted off. To renew the writing point, a test-tube, conical below, is fitted to the cone of the lead: the whole is held in warm water for a minute, when sufficient phosphorus flows out to form a new point.

Preparation of Phosphuretted Hydrogen.

Prepare phosphide of zinc by mixing together amorphous phosphorus with half its weight of powdered zinc, and gently heating the mixture in a hard glass tube through which a current of dry hydrogen or coal-gas passes. The tube and contents must be cooled in the current of gas. From the phosphide of zinc so prepared phosphuretted hydrogen may be readily obtained by means of dilute sulphuric acid or by boiling with caustic potash. The gas is, however, the non-spontaneously combustible kind. The spontaneously combustible gas may be obtained by taking a larger quantity of phosphide of zinc and dissolving it in warm dilute sulphuric acid.

Estimation of Phosphoric Acid.

A. **By the Modified Tin Process (Reynoso's).**—This method depends upon the fact that, when metallic tin is added in excess to a solution of a phosphate in nitric acid, the stannic acid formed by the oxidation of the metal combines with the phosphoric acid and completely removes it from solution. On filtering, therefore, we at once separate the bases which remain in solution, from the insoluble combination of stannic and phosphoric acids. In order to determine the amount of phosphoric acid contained in the tin oxide, the compound is dissolved in a small quantity of concentrated potash solution, when the two acids dissolve as meta-stannate and phosphate of potassium; the fluid is now saturated with sulphuretted hydrogen, a small quantity of pentasulphide of ammonium added, and, lastly, a slight excess of acetic acid. The sulphide of tin is then separated by filtration; all the phosphoric acid is contained in the filtrate, and its amount may be determined

by the ordinary method as ammonio-phosphate of magnesium. Two very good modifications of this method have been given.

Modification 1.—According to the first the substance is dissolved in nitric acid. When there are any difficulties in getting it into solution, dissolve it first in any convenient agent, then add excess of ammonia to the solution, which precipitates all the phosphoric acid, with most of the bases; well wash this precipitate; it will then be readily soluble in nitric acid.

If, for instance, a specimen of cast-iron is being analysed, it must be dissolved in aqua regia; if a refractory mineral, it must be attacked by alkalies, &c.

The nitric solution having been obtained (which should be free from chlorides), throw into it an indefinite quantity of pure tin; about four or five times the supposed weight of the phosphoric acid present may be employed. This tin passing to the state of stannic acid, under the influence of the nitric acid, carries down with it all the phosphoric acid, as well as a great portion of the iron and a little aluminium; wash at first by decantation and then on a filter, and place on one side the nitric solution, which is free from tin, but contains all the bases minus a portion of iron and aluminium. Then re-dissolve the precipitate in a small quantity of aqua regia, and, without troubling about the filaments of filter-paper, or the small portions of phosphate of tin which may remain undissolved, supersaturate with ammonia, and then add an excess of sulphide of ammonium. The stannic acid and phosphate of tin immediately dissolve, leaving a black precipitate of sulphide of iron containing aluminium; allow it to stand for an hour or two, and then filter, taking care to wash the precipitate with sulphide of ammonium to remove the last traces of tin. It is then only necessary to add sulphate of magnesium to the filtered liquid to obtain the characteristic precipitate of ammonio-phosphate of magnesium. Collect this on a filter, wash it first with sulphide of ammonium, then with ammoniacal water, and afterwards calcine in the ordinary manner.

The filter containing the sulphide of iron and aluminium is re-dissolved in nitric acid, and the filtered liquid is added to the original solution of the bases, which may then be separated in the ordinary way.

This method is both simple and rapid; it enables one to estimate the phosphoric acid contained in the most complicated mixtures, and then admits of the accurate separation of the bases.

Modification 2.—Obtain the phosphate in solution in nitric acid, as described above. Concentrate the solution and add the strongest nitric acid (boiling at 86° C.) The nitric acid solution is now in the highest possible state of concentration: on throwing a small quantity of tin into this solution, the metal is rapidly oxidised to stannic acid, and the supernatant liquid remains perfectly clear. The preliminary heating of the

solution is indispensable, since in the cold the metal is apt to become passive, when it completely resists the action of the acid. The precipitate is now dissolved in a small quantity of caustic potash, and saturated with sulphuretted hydrogen; on adding acetic acid in slight excess the sulphide of tin is precipitated. The precipitate is then separated by means of the Bunsen filter-pump, and the whole of the phosphoric acid is contained in the filtrate. After concentrating the solution, and again filtering from a minute precipitate of tin-sulphide, which invariably separates out (sulphide of tin being slightly soluble in solutions containing sulphuretted hydrogen), the phosphoric acid may be precipitated as the ammonio-magnesium salt, and weighed as pyrophosphate.

The amount of tin need not exceed four times the weight of the phosphoric acid present. This, however, is the minimum quantity that can be used with safety.

B. **Estimation of Phosphoric Acid by the Magnesium Process.**—The estimation of phosphoric acid in minerals containing fluorine, iron, and aluminium, is a matter of considerable difficulty. After dissolving in mineral acids, most authorities advise that the acid solution should be brought to dryness before proceeding to separate the calcium. Some analysts, however, neglect this part of the process, from the impression that it has no influence on the estimation of the phosphoric acid, and that it is only necessary when the siliceous matter is required for a full analysis. Mr. T. R. Ogilvie has instituted several experiments to show that this impression is an erroneous one. From them the following are selected:—

(1.) A gramme of Cambridge coprolites was dissolved in moderately strong hydrochloric acid, evaporated to dryness, the residue again dissolved in acid, the calcium separated with oxalate of ammonium, citric acid added to hold up iron and aluminium, the solution made alkaline with ammonia, and the phosphoric acid precipitated with "magnesia mixture." A perfectly granular precipitate was obtained, which, after standing for twelve hours, was washed, dried, ignited, and weighed, and found to be equivalent to 47·44 per cent tribasic phosphate of calcium.

(2.) Another gramme of the same coprolites was treated in exactly the same way, with the exception that the acid solution was *not* brought to dryness. The ammonio-phosphate of magnesium, as it gradually formed, presented the usual appearance; but, when stirred up after a few minutes, a white flocculent body was also observed. After standing for the usual time, the whole precipitate was collected, washed, dried, ignited, and weighed, and gave 53·04 per cent phosphate of calcium.

(3.) A third gramme was treated as in (2), with the difference that, after the addition of citric acid, the solution was made alkaline with ammonia,

and allowed to stand. In a short time a white flocculent precipitate formed, which was filtered, washed, dried, ignited, and weighed.

To the clear ammoniacal filtrate, "magnesia-mixture" was added; and a granular precipitate, free from any flocculent matter, was obtained, equivalent to 47·20 per cent phosphate of calcium. This closely corresponds with the result (viz., 47·44 per cent) got in (1) after evaporating to dryness.

The flocculent precipitate got by ammonia weighed 4·05 per cent. Had it not been removed, it would have been taken as ammonio-phosphate of magnesium, and, as such, been equivalent to 5·66 per cent phosphate of calcium; this, added to 47·20 per cent, gives 52·86 per cent, against 53·04 per cent found in (2) by weighing the flocculent precipitate along with the ammonio-phosphate of magnesium.

In these experiments, care was taken that the calcium was perfectly separated, and that sufficient citric acid was present to hold up iron and aluminium.

The precipitate which forms on the addition of ammonia to the citric acid solution when the material has not, at the outset of the process, been brought to dryness, consists of silica, alumina, and sesquioxide of iron as silicate, and, when carefully washed, is free from phosphoric acid. In the case of sombrerite, some ammonio-phosphate of magnesium would also come down, owing to the presence of a considerable quantity of magnesium in that mineral. But, with coprolites and other phosphatic minerals, which contain only minute quantities of magnesium, neither phosphoric acid nor magnesium is found, unless the flocculent precipitate is not filtered from the solution for a few hours.

All phosphatic minerals which contain fluorine, oxide of iron, and alumina, give this precipitate.

Those minerals containing fluorine, and only a trace of iron and aluminium, such as Canadian apatite and Spanish phosphorite, give no appreciable flocculent precipitate. A sample of sombrerite was also examined, but, as it was exceptionally free from iron and aluminium, it gave no flocculent precipitate.

It may be mentioned that, when coprolite, or other ferruginous phosphatic mineral, is moistened with sulphuric acid, gently heated, and the fluosilicic acid which forms driven off, then dissolved in hydrochloric acid, and the calcium removed without the solution being brought to dryness, no flocculent precipitate is got. And neither do superphosphates which have been prepared from these minerals give a precipitate.

It would thus seem that, in the analysis of the majority of the phosphatic minerals at present in use by manure manufacturers, special care must be taken to obtain a pure and perfectly granular precipitate of

ammonio-phosphate of magnesium, either by evaporating the acid solution to dryness, or by separating the precipitate which forms on the addition of ammonia to the solution containing citric acid; otherwise an erroneously high result is got.

C. **Estimation of Phosphoric Acid by the Uranium Process.**— In the analysis of manures, coprolites, bone-ash, and similar commercial substances, the magnesium process for estimating phosphoric acid is beset with so many difficulties, that it is worth while to look for some other method by which the same end can be attained without the expenditure of so much time and trouble. Mr. Sutton strongly recommends the uranium process, which he considers to be equally accurate with the magnesium process, and far preferable to it in readiness of application and general convenience. One of the chief advantages connected with the use of uranium as a means of estimating phosphoric acid in phosphates of calcium, &c., is that the presence of acids does not interfere with the result.

The metals which admit of this mode of determination are, so far as present experiments have proved, potassium, sodium, calcium, magnesium, iron, and aluminium; the two latter only, however, with modifications of the process as applied to the former. These modifications are given further on.

In the presence of potassium, sodium, magnesium, calcium, and barium, the following course must be adopted:—

The substance is to be dissolved if possible in acetic acid; if, however, this is not to be done, a nitric, hydrochloric, or sulphuric acid solution is admissible, taking the precaution to avoid any great excess of acid; add ammonia in excess, and re-dissolve the precipitate in acetic acid; in the presence of mineral acids it is advisable to add acetate of ammonium as well as acetic acid. Lastly, add a solution of acetate of uranium (best obtained by dissolving pure ammonio-carbonate of uranium in acetic acid) and heat to boiling, by which means the phosphoric acid is completely separated as phosphate of uranium and ammonium.

This precipitate is of a greenish-yellow colour and somewhat slimy in its nature; therefore in order to prevent the pores of the filter from being choked by it, it must be handled in the following manner:—After boiling, set aside on the sand-bath, and allow the precipitate to settle; when the supernatant liquid is clear, decant through the filter, pour water over the precipitate, and again boil for a few moments; decant as before, taking care that the precipitate has entirely subsided; repeat the process three or four times until the sliminess of the precipitate has given place to a feathery appearance, then pour it out upon the filter and complete the washing in the usual way.

The above process may be hastened somewhat by adding to the liquid in

which the precipitate is first suspended, after it has somewhat cooled, a few drops of chloroform; then vigorously stirring the liquid or boiling it up once or twice causes the precipitate to settle more rapidly.

The phosphate of uranium and ammonium thus obtained is totally insoluble in water and acetic acid, but easily so in mineral acids; the addition, however, of a sufficient excess of acetate of ammonium throws it down completely again on boiling. On burning the precipitate the ammonia is driven off, and a lemon-coloured phosphate of sesquioxide of uranium is obtained possessing the formula $2(Ur_2O_3),PO_5$. If, however, carbon or any reducing gas is present during the burning of the precipitate it is partly reduced to phosphate of protoxide of uranium, of a green colour; but on moistening it with nitric acid and again heating, the yellow colour of the higher oxide is reproduced.

It is therefore advisable in burning the precipitate to separate it from the filter, first burning the latter, then adding the former, and heating to redness until every trace of carbon is removed. As a precaution against partial reduction it is advisable in all cases to moisten the precipitate when cool with nitric acid, and again heat to redness. The burning may take place in an open platinum crucible, and as the precipitate is scarcely hygroscopic it may be weighed uncovered.

If it should be necessary to re-dissolve the precipitate in order to estimate the phosphoric acid afresh, the solution must first be preceded by melting the precipitate with a considerable excess of carbonate of sodium so as to convert the pyrophosphoric into tribasic phosphoric acid.

The composition of the phosphate of uranium is as follows:—

		Per cent.
$2Ur_2O_3$	285·6	80·01
PO_5	71·0	19·99
	356·6	100·00

Therefore one-fifth of the precipitate may be calculated as phosphoric acid.

This process has been used for the determination of phosphoric acid in guanos, the so-called superphosphates of lime, bone-ash, coprolite, &c., in above a hundred analyses, and in many of them the results controlled by other methods, without one instance of inaccuracy or failure. In the more delicate process of urinary analysis it has been found equally reliable.

Special Precautions to be taken when Iron is Present.—When a compound containing iron as well as phosphoric acid is submitted to analysis by the uranium process, the precipitate of phosphate of uranium invariably carries down a portion of iron with it. In this case the colour of the precipitate is altered to a dirty orange-yellow, and possesses a somewhat granular appearance. The quantity of iron depends in some measure upon the length of time the mixture has been kept at a boiling heat. If the

boiling be continued for about twenty minutes, the iron is entirely removed from the precipitate, and the solution is coloured red by acetate of sesquioxide of iron. The better way, however, is not to depend upon this mode of separation, but to reduce the sesquioxide of iron to protoxide, by means of protochloride of uranium.

The compound is to be dissolved in the smallest possible quantity of hydrochloric acid (at most 1½ ozs.) and the solution of protochloride of uranium added in sufficient quantity to produce a distinct green colour, or until one drop of sulphocyanide of potassium does not show a change to red. Now add ammonia in sufficient quantity to neutralise the free hydrochloric acid, making sure by throwing into the mixture a small piece of litmus paper. Add a solution of acetate of uranium and free acid, together with a few drops of acetate of protoxide of uranium (obtained by precipitating the protochloride with ammonia and re-dissolving in warm acetic acid), to insure the presence of sufficient protoxide, and heat to boiling.

The mixture must now possess a distinct greenish colour, not a dirty tinge, which shows the presence of undissolved protoxide of uranium. Put aside until the precipitate has settled; when this has *completely* taken place decant the supernatant liquid through the filter; pour hot water over the precipitate, adding some chloride of ammonium, and boil again; repeat the operation once more, and the washing is complete; the precipitate may now be thrown upon the filter, dried, and burned as described at the commencement of this process.

Preparation of Protochloride of Uranium.—It may not be amiss here to give the best method of preparing a solution of protochloride of uranium, which promises to be a most serviceable reducing agent in analysis.

Ammonio-carbonate of uranium is to be dissolved in about twice as much hydrochloric acid (diluted with an equal quantity of water) as is necessary for solution. A concentrated solution of bichloride of platinum is added in the proportion of about two drops to each ounce of uranium-salt; fine shreds of copper are then to be added in excess, and the mixture boiled for ten or fifteen minutes, or until the liquid assumes a distinct green colour, and the sesquichloride of uranium is reduced to protochloride.

In order to remove the protochloride of copper from the solution it is now to be boiled until, on adding a few drops to some water, an immediate precipitate is produced. Half-an-hour's boiling is generally sufficient to attain this end. The solution is then to be diluted pretty freely with water, and set aside to cool. When perfectly cold, the copper will in great measure be separated. Sulphuretted hydrogen, however, must be passed through the filtered solution till every trace of copper is precipitated and the liquid smells strongly of the acid.

The filtered liquid is now to be poured into a porcelain capsule, and evaporated at a boiling heat, adding some considerable quantity of chloride

of ammonium to prevent the precipitation of protoxide and sulphide of uranium, which would otherwise be the case.

As the sulphuretted hydrogen is very difficult to remove, the evaporation must be carried on till the liquid corresponding to each ounce of the original uranium salt is reduced to about three ounces. It is absolutely necessary that every trace be removed. If at the end of the operation a precipitate has occurred, it may be dissolved in a little concentrated hydrochloric acid after the clear green liquid has been poured off, and the two solutions mixed and kept for use.

The solution so prepared contains chloride of ammonium, which is of no consequence for the purpose here contemplated; neither is it any hindrance to the preparation of the pure crystals of protochloride of uranium, as on adding excess of ammonia the uranium is precipitated and can be re-dissolved.

The value of this solution as a means of reducing sesquioxide to protoxide of iron (and probably other higher oxides to lower) cannot be too highly estimated, for at ordinary temperatures it takes place speedily, but at boiling heat immediately: moreover, the change is visible to the eye, for the reddish colour of the solution gives place to green, and so long as this is the case the iron exists in the form of protoxide.

The delicacy of this reaction may be readily seen, if to a solution of sesquichloride of iron a drop or two of sulphocyanide of potassium be added, which produces a blood-red colour: add now a few drops of the uranium solution, and immediately the colour turns to green, showing that a reduction has taken place; this reaction may be made over and over again by adding first iron and then uranium.

D. Estimation of Phosphoric Acid by the Bismuth Process.—Take 2 grms. of the very finely pulverised phosphorite; put the weighed mineral into a flask, or beaker glass, and pour over it about 7 c.c. of nitric acid free from chlorine, and of 1·25 sp. gr. Heat the vessel and its contents for about half an hour nearly to the boiling-point, dilute with pure distilled water and filter; add to the well-washed filtrate as much water as will suffice to make up a quantity of 500 c.c. Take 100 c.c. of this liquid, representing 0·4 grm. of phosphorite; add another 100 c.c. of pure distilled water, heat to the boiling-point, and precipitate the hot fluid by the addition of a solution of nitrate of bismuth prepared in the following manner:—

Take crystallised nitrate of bismuth, dissolve in water; add as much nitric acid as is required to prevent precipitation on the addition of more water; make up the solution in such a manner as to obtain a litre of fluid containing 26 grms. of bismuth.

The precipitate, occasioned by the addition of the bismuth solution to the solution of phosphorite, is left standing till quite cold, and is then filtered

off, the precipitate being washed with cold water. Next, the phosphate of bismuth is dissolved, while on the filter, in a few drops of hydrochloric acid, and the solution is treated with ammonia and sulphide of ammonium, and gently heated, until all the bismuth has been converted into sulphide. When this has been effected, the liquid is acidified with acetic acid, and heated to near the boiling-point; the precipitate is then collected on a filter, the last traces of sulphuretted hydrogen being eliminated by a few drops of chlorine water.

The phosphoric acid is estimated in the acetic acid solution by the uranium process.

E. **Estimation of Phosphoric Acid by the Lead Process.**—For the estimation of phosphoric acid in coprolite or sombrerite, which contains a considerable amount of iron and aluminium, besides calcium, magnesium, &c., Mr. Warington considers that very few of the processes usually recommended for the determination of phosphoric acid are here applicable. The molybdic acid method is inadmissible from the large amount of phosphoric acid to be determined. The mercurial method fails owing to the presence of aluminium. The uranium method can be employed only if the iron be previously reduced by means of protochloride of uranium. The tin method is free from all these objections, and is no doubt, when carefully conducted, an excellent process, but the time it takes up is considerable. The process which Mr. Warington prefers is given below.

The subject divides itself into two parts, the estimation of phosphoric acid and of the alkaline earths, and the estimation of iron and aluminium.

The nitric acid solution* of the mineral, previously freed from silica in the usual way, is treated cautiously with dilute ammonia to remove all unnecessary excess of acid; the clear liquid is then treated in one of two ways; either an excess of neutral acetate of lead is added, or the solution is treated with nitrate of lead, and digested with successive portions of finely-powdered litharge till slightly alkaline, the liquid in this case being finally acidified with a few drops of acetic acid. The former plan is generally to be preferred, though the precipitate is considerably more bulky, as only a portion of the iron, and probably none of the aluminium, is in this case precipitated with the phosphoric acid.

The precipitated phosphate of lead is warmed for some minutes to induce aggregation, and then thoroughly washed by decantation, the washings being filtered. The washing water should be slightly warm, and contain a little acetate of ammonium, otherwise the filtrate is apt to be turbid.

* When nitric acid alone is used to effect the solution of a coprolite a trace of phosphoric acid is sometimes left with the silica; it is therefore safest to dissolve in hydrochloric acid, and after evaporation to dryness to re-dissolve with nitric acid.

There are several ways of treating the precipitate. It may be dissolved in nitric acid (which for this purpose must not be too weak), the solution diluted and the lead precipitated by means of sulphuretted hydrogen; or the nitric solution may be treated with an excess of sulphuric acid and the lead precipitated as sulphate. The first plan is unexceptionable and yields excellent results; the necessary dilution entails, however, a subsequent concentration which occupies some time. If acetate of lead has been used, the best plan for ordinary purposes is to treat the phosphate of lead with oxalic acid and a few drops of oxalate of potassium. The decomposition is rapid and complete; the oxalate of lead may after a short time be separated by filtration. Oxalic acid does not perfectly decompose the highly aggregated precipitate obtained with nitrate of lead and litharge. The action of sulphuric acid on the precipitate is incomplete, whether nitrate or acetate of lead has been employed. Oxalate of lead is nearly insoluble in oxalic acid; its solution, if treated with sulphuretted hydrogen water, appears only very slightly discoloured when looking through a depth of several inches.

The lead being separated, the solution now contains the whole of the phosphoric acid with a little iron; some citric acid is added and an excess of ammonia; the clear solution is finally treated with "magnesia mixture," and the phosphoric acid separated in the usual way.

The calcium, magnesium, and alkalies are readily determined in the original filtrate from the phosphate of lead, the excess of lead being first precipitated by means of sulphuretted hydrogen. A little citric acid must be added before the solution is made ammoniacal for the determination of the magnesium, to hold in solution the iron and aluminium. This method has the advantage of speed, and admits of the convenient determination of all the bases except iron and aluminium. It is applicable to the analysis of all the phosphates employed in agriculture.

F. Estimation of Phosphoric Acid by Means of Mercury.—The nitric acid solution of the phosphate is evaporated to dryness with excess of metallic mercury, the residue collected and washed, mixed when dry with carbonate of sodium, and very gradually heated to fusion. The fused mass is dissolved in water, neutralised with acid, and the phosphoric acid estimated as ammonio-phosphate of magnesium. This method gives very accurate results.

G. Estimation of Phosphoric Acid by Means of Iron.—Dissolve the phosphate in acid, add to the solution perchloride of iron, and then excess of acetate of sodium. Boil for some time till the whole of the iron is precipitated. The whole of the phosphoric acid will come down with the iron.

If the substance under analysis is free from iron or aluminium, the

perchloride of iron should be added in known quantities from a standard solution. Upon now washing, drying, and weighing the precipitate, the excess of weight over that due to the sesquioxide of iron present represents phosphoric acid.

If, however, iron or aluminium are present, the precipitate is dissolved in hydrochloric acid, citric acid is added, and the phosphoric acid precipitated by "magnesia mixture." Were it not for the inconvenience of working with so large a bulk of iron precipitate this process would leave little to be desired.

H. Estimation of Phosphoric Acid by the Molybdic Acid Process.—To the nitric acid solution of the phosphate, add a large excess of solution of molybdate of ammonium in nitric acid, a yellow precipitate of phosphomolybdate of ammonium falls down, which is almost insoluble in acids. Allow the mixture to stand in a warm place for a day, filter, and wash with a dilute acid solution of molybdate of ammonium. Dissolve the precipitate in ammonia, and to the clear solution add "magnesia mixture." This process is very accurate when small quantities of phosphoric acid have to be estimated in the presence of large quantities of iron or aluminium. No arsenic or silicic acid must be present, as it would precipitate with the molybdenum solution, and afterwards with the magnesia mixture. According to Nuntzinger's analysis of phosphomolybdate of ammonium, after drying at 212° F., it contains 3·577 per cent of oxide of ammonium, 3·962 per cent of phosphoric acid, and 92·461 per cent of molybdic acid.

Recovery of Molybdic Acid from the above Operation.—The acid liquors, the filtrates from the yellow precipitate, are mixed with the ammoniacal wash-waters from the ammonio-phosphate of magnesium precipitates, and, in addition, there is added phosphate of sodium solution, in the proportion of 1 part of phosphoric acid to 30 of molybdic acid; after which, the fluid is left at rest for twenty-four hours in a warm place. The precipitate is collected on a filter and washed, until the filtrate begins to run slightly turbid; the precipitate is next dried in a water-bath, then dissolved in ammonia, and the solution poured into nitric acid in which 2 or 3 parts of pure magnesia have been dissolved. The ensuing precipitate of ammonio-phosphate of magnesium is next removed; and, after having been standing for some time, in order to give time for a small quantity of phosphate of molybdenum to settle, the solution is fit for use again as molybdate of ammonium.

I. Estimation of Phosphoric Acid by Means of Oxalic Acid.—Dissolve the phosphorite in acid, and separate the silica in the usual way. Add dilute ammonia carefully until a slight permanent opalescence is produced, but be careful not to neutralise. Add just sufficient dilute oxalic acid to remove this opalescence and allow it to stand. The solution will

become yellow if iron is present. Now precipitate the calcium by an excess of oxalate of ammonium, warm, and filter. Evaporate the filtrate, add citric acid to hold the iron and aluminium in solution, then add ammonia in excess and "magnesia mixture" to precipitate the phosphoric acid. The oxalate of calcium cannot be used to estimate the amount of calcium present, for there will be a slight deficiency owing to its solubility in oxalic acid.

The ammonio-phosphate of magnesium always contains a trace of oxalate of calcium, insufficient, however, to vitiate the results for ordinary purposes. When great accuracy is required the best plan is to re-dissolve the precipitate in dilute acetic acid, filter from oxalate of calcium, and then re-precipitate and weigh as usual.

K. Estimation of Phosphoric Acid as Phosphate of Calcium.—This is a very common method of approximately determining the value of guano, and sometimes bone-ash. The results are never very exact, but the method is simple and speedy, and will frequently give all the information that is required. The phosphate is dissolved in acid, and to the clear solution ammonia in excess is added; the precipitated phosphate of calcium is collected and weighed. With guanos which contain phosphate of calcium and alkaline salts the results are tolerably accurate, but in the case of bone-ash the precipitated phosphate of calcium contains lime mechanically carried down. The results are quite unreliable in the case of coprolites, although this method is sometimes used in their valuation.

L. Estimation of Phosphoric Acid by Volatilisation.—I have not experimentally verified this process, but as the principle is novel, and appears likely to be of use in some cases, it may not be out of place to insert an abstract of it along with other processes. The author is Dr. Th. Schlœsing.

By heating to whiteness a mixture of carbon, silica, and phosphate of calcium, magnesium, or aluminium, the whole of the phosphorus is not extracted, owing to the unavoidable imperfection in the mixture. To avoid this drawback the carbon is replaced by a current of reducing gas, and the silica and phosphate are intimately mixed by dissolving the latter in very little nitric acid, and by adding silica to the hot liquid until it refuses to absorb more. By drying on a sand-bath, and heating to redness, a mixture is obtained which does not adhere to platinum, and which can be transferred when necessary with no loss whatever.

As phosphorus attacks platinum, and as it is necessary to preserve the silicate in its integrity, which could not consequently be placed in contact with porcelain, the mixture of phosphate and silica is transferred to a charcoal boat, to introduce it afterwards into a tube of Bayeux porcelain. This kind of boat is made by pouring a paste of carbonised sugar and syrup through a tube made of blotting-paper; after a few minutes remove the

excess affixed to the paper; next dry, and then make red hot; then cut the tube into two half cylinders, and close the ends with a paste more solid than the first. The tube may be heated in various ways, but gas is the best, as then it is not necessary to preserve the tube from contact with the combustible, and the same tube serves for several operations. Four strong blowpipes should be arranged, vertically, at equal distances, within a space of 8 centimetres, and projecting their flames on the porcelain tube, whose heated part, about 10 centimetres, is surrounded by platinum foil, and placed in a muffle composed simply of a few refractory bricks. In seven or eight minutes the tube reaches white heat.

The most suitable reducing gas is carbonic oxide, which is a sufficient reducer even for phosphoric acid; it must be dry, as phosphorus decomposes water at red heat, and should retain little carbonic acid, which might interfere with its reducing power.

In two experiments made by Dr. Schlœsing, a mixture of phosphate of magnesium and silica, containing 0·062 grm. of phosphoric acid, lost 0·063; and a mixture of phosphates of aluminium and calcium with silica, containing 0·124 grm. of phosphoric acid, lost 0·123 grm. The silicate produced was agglomerated in the form of a porous scoria.

In these two experiments the heating lasted half an hour, and each consumed one and a-half litres of oxide of carbon.

When phosphates are free from aluminium, the silicates produced abandon their bases to hot nitric acid, although they contain some excess of silica and have undergone a high temperature. When phosphates contain aluminium the silicates are again destroyed by digestion with potash at 150° to 200° C.; thus, in both cases, the bases can be easily determined after the removal of the phosphoric acid.

When the phosphorus has been set at liberty, it may be collected and estimated directly. The porcelain tube may be luted on to a thin silver tube containing metallic copper, and heated to dull redness. The silver will not be attacked, but the copper will absorb the whole of the phosphorus, the quantity of which will be indicated by the increase of weight of the silver tube. But we do not in this way get a compound so well defined as might be desired; hence the author prefers transforming the phosphorus into a phosphate which should realise this condition. The gaseous current from the porcelain tube is passed through a bulb tube containing a solution of nitrate of silver. The whole of the phosphorus condenses in it, forming black phosphide of silver, and some phosphate dissolved by the displaced nitric acid. The bulb tube should be heated in a water-bath to 80° or 90° C.; for the true combination of carbonic oxide and phosphorus mentioned by Berzelius only abandons all its phosphorus with the aid of heat. The silver liquid is decanted into a platinum capsule and evaporated; on the

residue pour hot nitric acid with which the bulbs have been washed; all the phosphorus is thus converted into phosphate; evaporate to dryness, heat until the excess of nitrate of silver is fused, and no perceptible acid vapours are disengaged. Under these conditions, the phosphoric acid unites with exactly three equivalents of silver, constituting the tribasic phosphate. The resulting salt is washed by simple decantation, then dried and weighed.

Phosphate of silver possesses two advantages in analytical processes; its equivalent is very heavy, and its composition is rapidly verified by the estimation of silver. A little phosphorus is condensed in the porcelain tube, but it is red phosphorus, emitting no vapour when cold, and it may be recovered without loss by rinsing out the tube with nitrate of silver and then with nitric acid; these washings are added to the contents of the bulbs.

The production of tribasic phosphate of silver in presence of fused nitrate of silver is not limited to the instance just given; phosphates of ammonium, potassium, and sodium behave like pure phosphoric acid. This, then, is a very sure method of estimating phosphoric by phosphate of silver, either when alone or accompanied by an alkali, but in the absence of any earthy or metallic base.

M. **Estimation of Phosphoric Acid Volumetrically.**—No volumetric process for estimating phosphoric acid is sufficiently good for very accurate work, but owing to the ease with which these estimations are made and the great advantage of their rapidity when many determinations are to be made every day, it is generally felt that in commercial analyses it is allowable to sacrifice a certain amount of accuracy for the sake of speed, provided always that the errors of experiment are not sufficiently great as to be of commercial consequence. Mr. Burnard has been in the habit of employing a modification of the well-known uranium volumetric process in the analysis of phosphatic manures, and in the following description he has drawn attention to several precautions which are necessary to ensure the requisite degree of accuracy, for often with the greatest care as to uniformity of volume in samples tested, it is frequently doubtful when the point of colouration is obtained. In two determinations of the same sample made side by side it is seldom that complete uniformity of results are obtained. Much depends on the size of the drop falling into the little pool of ferrocyanide—something in the manner in which the said drop falls; while in all cases *time* is an essential element in the question. If testing be continued until the brown colouration is evident, the result will be far too high. To prove this, let the operator in reaching the desired indication cover over his slab (to prevent drying) and leave it so some hours, say until next morning, when he will find the point to be five or six

units below that indicated over night. But even now there is much uncertainty, for if he has (as he should always have) tried two side by side, he will frequently be perplexed in making his decision. By adopting the following method all doubt is dissipated, and much greater accuracy obtained.

If the composition of the substance be quite unknown, a preliminary examination is made, which soon shows the probable range of its percentage of phosphoric acid. But in general this is unnecessary. A plain porcelain slab is used, pits or indentations for the pools being objectionable, as hindering due access of light to the body of the pool. To prevent flowing about, a ring of cork, giving a clear space of ⅜ of an inch, pressed on some hard tallow and then on the slab, leaves a faint but effectual wall of grease.

The method may be best explained as follows, giving an actual determination by way of illustration. Three portions of the same solution, being each 100 septems, were taken and tried side by side on the same slab.

No. 1.—26	28	30	32	34	Septems.*
No. 2.—25	27	29	31	33	"
No. 3.—24	25	26	27	28	"

Now, at the conclusion of the actual testing, not one exhibited the slightest trace of brown colouration; they all appeared precisely alike. They were then covered over and left until the morning, when one only, viz., 34, showed the red-brown colour, and that as an intense bright eye in the centre of the pool.

Now, following out the modification here proposed, the slab was carefully put on a levelled stand before a fire, and the spots dried by radiant heat falling on their surfaces; gently drying in this way being preferable to any other, for rising from below the heat disturbs the settlement of the precipitate. When dry, and the slab just warm, water was carefully dropped on each spot, so as to dissolve the dried-up ferrocyanide, when, as if by magic, although on the dried slab there was not a trace of brown visible, the truth was revealed, and the reading became—

No. 1.—30	stood as the	number.
No. 2.—29	do.	do.
No. 3.—29	do.	do.

At the time of testing there was no exhibition of colour; next morning 34 stood revealed; but on drying and re-dissolving, as explained, 29 was unquestionably the number. It is obvious that, while a precipitate may be so slight as to render the colouration of a small pool difficult, yet by its

* In the above each number is intended to represent a thin pool of ferrocyanide of potassium, of about ⅜ inch diameter; and also in each case the number of septems of nitrate of uranium employed.

settling down on the white slab it is immediately revealed on dissolving away the crust covering it.

Volumetric Estimation of Phosphoric Acid by Means of Lead.—The phosphate is either dissolved in water or dilute nitric acid, the solution mixed with excess of lead solution and acetate of sodium. Tribasic phosphate of lead precipitates; this is allowed to subside, is washed and filtered, and the excess of lead in the filtrate ascertained by the volumetric process described at pp. 212, 213. Each c.c. of lead solution corresponds to 0·00476 grains of phosphoric acid.

The filtration and washing of phosphate of lead is not so easy as in the case of sulphate of lead, and may be avoided by allowing the precipitate to subside in a graduated vessel, and then removing a portion of the clear supernatant liquor by means of the pipette. By ascertaining the amount of lead therein contained, the whole amount may be calculated.

The presence of calcium does not interfere with these reactions, and bones, guano, or other manures may be analysed in this way without trouble. They are calcined to destroy organic matters, the residue washed, and any alkaline phosphates estimated in the filtrate, while the insoluble portion is dissolved in dilute nitric acid, filtered from the sand, &c., and excess of acetate of sodium added. Iron and aluminium are precipitated on the addition of acetate of sodium, and carry down with them some phosphoric acid. If oxide of iron alone is present, the precipitated phosphate of iron may be filtered off, dissolved in hydrochloric acid, reduced by zinc, and the protosalt of iron estimated by permanganate of potash, when the peroxide of iron will give by calculation the amount of phosphoric acid it was originally combined with in the precipitate. This may be safely done, as it is hardly ever probable that any manures contain excess of oxide of iron.

0·247 grm. of phosphate of sodium was mixed with chloride of calcium, acetic acid, and acetate of sodium, and 12 c.c. of lead solution added. The excess of lead in the filtrate amounted to 1·7 c.c of bichromate of potassium solution, which leaves (12 − 1·7) 10·3 centimetres of lead solution, or 0·049 grm., or 19·83 per cent of phosphoric acid: calculated it should have been 19·89.

0·3547 grm. of phosphate of sodium and nitrate of magnesium required 20 c.c. lead solution, 5 c.c. chrome solution, being equal to 0·0714 grm., or 20·13 per cent of phosphoric acid.

A specimen of Peruvian guano examined in this manner gave—

Phosphate of sodium	0·56 per cent.
Phosphate of iron	1·35 „
Phosphate of calcium	23·09 „

Fresh bone-black gave—

Phosphate of calcium	72·10 per cent.
Carbonate of calcium	6·83 „
Silica	2·92 „
Loss by calcination (carbon and water)	18·15 „
	100·00

Bone-meal of fresh bones gave—

Organic matter	43·77 per cent.
Carbonate of calcium	4·34 „
Silica	2·20 „
Phosphate of calcium	49·69 „
	100·00

Volumetric Estimation of Phosphoric Acid in Superphosphates.—Mr. Burnard has also described another volumetric process, which is exceedingly simple and has afforded satisfactory results. It is not suitable in all cases, but may be applied to the determination of the phosphoric acid in the great majority of the so-called superphosphates; its value being increased, moreover, by the fact that it necessarily involves the estimation of the free acid in the manure. Suppose a superphosphate made in the usual manner; in such a manure the bone phosphate may be measured by the quantity of sulphuric acid employed in its solution. Extract all that is soluble in water from 100 grains of the manure, and divide it into two equal volumes of one thousand septems each, in beakers of the same dimensions. Into one drop a standard solution of carbonate of sodium from a burette, when, as is well known, a precipitation of bone phosphate occurs; this, however, on gently moving with a stirrer is re-dissolved; continue to drop in until there is a faint trace of a permanent precipitate, which may be the better detected by comparison with the other volume in the second beaker. When sufficient carbonate of sodium has been added, then, after duly noting the number of septems employed, an additional septem may be dropped in, when a decided milkiness and agitation will be manifest. The number of septems thus employed is the measure of the free acid existing in the manure. A little practice will enable the operator to very nicely determine the point of incipient precipitation. Now throw in a piece of litmus paper; if blue it instantly becomes red, and then continue the soda dropping until the red litmus becomes nearly blue. A few minutes repose will allow sufficient time for the precipitate to somewhat settle down, leaving a clear space above; into this a drop of carbonate of sodium solution may be carefully let down, when, if further precipitation occurs, more carbonate may be added, the whole stirred, and allowed again to subside. In practice it is found that the litmus should be brought to a decided but not to a deep blue.

Now the further volume of the standard solution of carbonate of sodium employed is the measure of the sulphuric acid economically employed in the manure, and is therefore the measure of the amount of the phosphoric acid in solution.

In comparative determinations, this process has given results nearly constantly one-half per cent too low.

Estimation of "Reduced" Phosphates in Superphosphate of Lime.

In the analysis of superphosphate of lime for agricultural purposes, the money value is based upon the amount of phosphate present which is soluble in water. But it frequently happens that on keeping, a process of "reduction," or going back, takes place; so that whilst a sample of freshly prepared superphosphate may contain, say, 25 per cent of soluble phosphate, the same sample after being kept for some time may only contain 22 or 23 per cent. It is impossible for the manufacturer to calculate the amount of this retrogression, and hence the discrepancies in the amount of soluble phosphate estimated by the seller and the buyer give rise to frequent disputes; and as from the nature of the action the seller's estimate must always be the highest, there is a tendency to throw discredit upon his analysis. The manufacturer considers it unjust that he should have expended time and money in producing soluble phosphate, which, owing to this reducing action, is valued at only about one-third the price it ought to fetch; whilst the buyer, who measures the value of a superphosphate by the amount soluble in water, naturally objects to pay for more soluble phosphate than his analyst certifies is present.

To avoid these frequent disputes, it is becoming the custom to express the amount of this reduced phosphate in an analysis of superphosphate, and many methods have been proposed for the purpose of estimating it with accuracy. The point is to find some reagent which does not affect the undecomposed coprolite (that being the mineral now more especially considered); dilute acids, such as acetic, citric, and oxalic (the latter least so), are objectionable on this account. The best plan is that in which oxalate of ammonium is employed. The process is carried out in the following manner:—Take about 1½ grms. of superphosphate, extract the soluble part with cold water, and, afterwards, with boiling water; wash the insoluble residue on the filter into a beaker, boil for about half-an-hour with oxalate of ammonium and about two drops of oxalic acid, so as to have a slight acid reaction; (this is done in order to keep the phosphate of magnesium in solution). Then filter; the filtrate contains the phosphates of calcium and magnesium, and, perhaps, a little phosphate of iron and aluminium. To the filtrate add tartaric acid, ammonia, and the magnesia mixture, weigh the precipitate, and estimate the phosphoric acid as $Ca_3(PO_4)_2$;

wash the insoluble residue on the filter into a beaker, boil for about one hour with sulphide of ammonium and a few drops of ammonia, filter, &c.; to the filtrate add the magnesia mixture, and calculate the results in the same manner as the reduced phosphates of calcium and magnesium.

Oxalate of ammonium is used, as being a perfectly neutral salt; it is altogether unlikely to decompose a perfectly mineralised substance like coprolite. As well known, the decomposition of gelatinous phosphate of calcium by oxalate of ammonium is a quantitative reaction, which takes place at once, the only necessity for boiling being to assist the subsequent filtration. Boiling for ten minutes is sufficient to effect this object, while the oxalate does not, under these circumstances, attack the coprolite to any material extent.

Mr. Sibson has tried the following experiments on this process:—25 grains of Cambridge coprolite are boiled, with an equal weight of oxalate of ammonium, in 2 ozs. of water, for ten minutes, and filtered; the filtrate acidified with hydrochloric acid, and made alkaline with ammonia (merely to ensure the presence of chloride of ammonium), and ammoniacal sulphate of magnesium added. No precipitate will probably be obtained; but, *if it be obtained*, it is not conclusive of the presence of phosphoric acid; and great errors may be made if a precipitate in this place be accepted as phosphate of magnesium and ammonium. After standing for two hours, the small precipitate is collected (which often resembles the phosphate closely, but consists of oxalate of magnesium, which sometimes separates from a concentrated solution, and a little oxide of iron) and re-dissolved in hydrochloric acid, citric acid added, and re-precipitated with ammonia. A precipitate, if now obtained, consists of phosphate of magnesium and ammonium only, and if burned and weighed as phosphate of magnesium in the usual way, will be found to amount to less than 0·5 per cent, calculated as bone-earth. This was found to be the case with coprolite ground as fine as it is possible to get it for analysis; but with coprolite in the state usually employed by manufacturers, no weighable quantity of phosphate of magnesium is found after standing three hours; 0·5 per cent of phosphate of calcium is therefore the utmost error that can be made by this process under proper management.

In the case of a superphosphate containing reduced phosphate, and treated as above, after having first extracted the soluble phosphate by cold water, the phosphate of magnesium calculated as bone-earth will represent the phosphate so reduced.

Separation of Phosphoric Acid from Aluminium.

To the acid solution of phosphate of aluminium add caustic soda in excess, digest for some time at a gentle heat, and separate the clear liquid

by decantation and filtration. To the solution add chloride of barium cautiously, till no more precipitate of phosphate of barium is produced, then add carbonate of sodium to remove the excess of barium, and lastly some more caustic soda; warm and filter. The phosphoric acid will be in the precipitate as phosphate of barium, together with carbonate of barium, and the aluminium will remain in the filtrate, from which it may be separated in the usual way.

Another excellent method of separating phosphoric acid from aluminium is to add to the solution bichloride of tin, boil, and precipitate all the oxide of tin in combination with phosphoric acid, by means of sulphate of sodium. If sesquioxide of iron is also present in the liquid a certain quantity will be precipitated at the same time.

Phosphoric acid may also be separated from aluminium by silicate of potassium. To the acid solution containing phosphate of aluminium add caustic soda in excess, digest for some time and filter; then add an excess of solution of silicate of potassium, which occasions the formation of a bulky precipitate of silicate of aluminium; collect this on a filter and wash. Acidify the filtrate with hydrochloric acid and supersaturate with ammonia to precipitate as far as possible excess of silica. Filter off and concentrate the solution, and add "magnesia mixture." This occasions the formation of a bulky precipitate, in part flocculent, in part crystalline. The whole is acidified with hydrochloric acid, which dissolves the crystalline and leaves the flocculent part of the precipitate. The liquid is filtered off, supersaturated with ammonia, and left twenty-four hours. The ammonio-phosphate of magnesium which separates is highly crystalline.

Separation of Phosphoric Acid from Bases in general.

A good method of separating phosphoric acid from bases consists in dissolving the substance to be analysed in a small quantity of nitric acid, and adding to the solution, first nitrate of silver, then carbonate of silver, and well shaking. All the phosphoric acid then combines with the oxide of silver and is precipitated, whilst the bases remain in solution and may be freed from the excess of silver by means of hydrochloric acid.

Separation of Phosphorus from Iron.

In the chapter on Iron (p. 99) mention has been made of several processes of estimating phosphorus in iron. The following are the processes referred to at p. 109.

Abel's Process.—50 grains of iron borings are acted on with warm nitrohydrochloric acid in a flask with a long neck, and after complete solution of the metal the contents of the flask are transferred to a porcelain basin and evaporated to dryness; the residue is moistened with concen-

trated hydrochloric acid and again evaporated, so as thoroughly to expel nitric acid. The residue thus obtained is dissolved in hydrochloric acid, the solution diluted, filtered, nearly neutralised with carbonate of ammonium, and the iron in solution reduced to protoxide by the addition of sulphite of ammonium to the gently heated liquid, and the subsequent careful addition of dilute sulphuric acid to expel excess of sulphurous acid. Acetate of ammonium and a few drops of solution of sesquichloride of iron are then added and the liquid boiled, when the phosphoric acid is precipitated as basic phosphate of sesquioxide of iron with some basic acetate. The liquid is rapidly filtered with as little exposure to air as possible, the precipitate is slightly washed, and dissolved in hydrochloric acid, the solution neutralised with carbonate of ammonium, and a mixture of ammonia and sulphide of ammonium added; it is then gently heated to ensure the conversion of the phosphate into sulphide of iron. The latter is afterwards removed by filtration, washed with dilute sulphide of ammonium, and the phosphoric acid is precipitated from the solution as ammonio-phosphate of magnesium, and weighed as pyrophosphate of magnesium.

Spiller's Process.—This is a modification of the above, and consists in dispensing altogether with the acetic treatment. After having dissolved the metallic iron in *red* nitrohydrochloric acid, drop into the flask containing the solution a few pieces of solid carbonate of ammonium, which, by causing an effervescence in the liquid, will aid in the expulsion of nitrous vapours. The great excess of acid should now be driven off by evaporation, and the diluted solution neutralised with ammonia or carbonate of ammonium. Bisulphite of ammonium is then added to effect the reduction of the sesquichloride of iron, and the excess of the latter having been driven off by heat, the solution is allowed to cool to 70° F., and a cold aqueous solution of sesquicarbonate of ammonium is added until the precipitate, at first red, assumes a greenish hue—a sign that some of the protocarbonate of iron is also thrown down. The whole of the phosphorus is contained in the precipitate thus obtained. It is unnecessary to pay particular attention to the thorough expulsion of the excess of sulphurous acid before proceeding to the use of the alkaline carbonate.

Preparation of Phosphorous Acid.

Phosphorous acid is a useful reducing agent, and has been recommended in previous chapters as one of the reagents to be employed in the separation of metals from one another. It is prepared in a sufficiently pure state for this purpose as follows:—Introduce a number of separate sticks of phosphorus into glass tubes an inch long, open above and below, but drawn out funnel-shaped at the bottom; these tubes being arranged in a funnel, and the funnel inserted into a bottle which stands in a dish containing

water. The whole arrangement is covered with a bell-jar, but in such a manner as to give access to the external air, which, however, should not be very warm. The acid which collects in the bottle is equal to about three times the weight of the phosphorus consumed. It is a mixture of about 1 atom of phosphorous acid and 4 atoms of phosphoric acid.

NITROGEN.

Estimation of Nitrogen by Weight.

Bunsen has given a method of analysing nitrates and nitrites which renders it possible to determine all the constituents of the salt in a single analysis. This method consists essentially in igniting the salt in an atmosphere of nitrogen gas, absorbing the oxygen evolved by metallic copper, and collecting the water in a chloride of calcium tube. The nitrogen in the salt is given by the loss of weight in the apparatus.

In those analyses of nitrates or nitrites in which it is only desired to determine the nitrogen, Dr. Wolcott Gibbs recommends the following modification, which may be employed with advantage:—

A hard glass tube about six inches in length is sealed at one end, and its volume determined by filling it with mercury and pouring this into a graduated vessel. The tube is to be carefully dried and weighed with a good cork; it is then to be filled with finely divided metallic copper, prepared by the reduction of the oxide, so as to enable the operator to judge of the quantity necessary. The salt to be analysed is then weighed and mixed with the metallic copper, either in a mortar or with a mixing wire in the tube, and the tube with its contents and cork is again weighed. The weight of the copper employed is thus known, and its volume may then be found by dividing this weight by the density of metallic copper. A weighed chloride of calcium tube is then adjusted as in organic analysis, and the combustion-tube is heated in the usual manner. When the combustion is finished, the open end of the chloride of calcium tube is sealed with the blowpipe flame, and the combustion-tube allowed to become perfectly cold. The chloride tube is then removed and weighed, and the combustion-tube also weighed with its cork. The increasing weight of the chloride of calcium tube gives the amount of moisture in the copper and the water in the salt analysed. The loss of weight in the combustion-tube gives the nitrogen in the salt after correction for the oxygen in the tube, for the moisture in the copper, and for the water in the salt. The correction for the oxygen in the combustion absorbed by the copper is easily found, with a sufficiently close approximation, by subtracting the volume of the copper from that of the tube, finding the weight of the residual air, taking one-fifth of this as oxygen, and considering the whole of this oxygen as

absorbed by the copper. A piece of asbestos may be placed between the copper and the cork with advantage; but this renders an additional correction necessary.

In two analyses executed by this method—in the first, a sample of pure saltpetre gave 13·86 per cent nitrogen, theory requiring 13·86 per cent; in the second, a specimen of the commercial salt gave 13·7 per cent nitrogen, while the same salt analysed by Simpson's method, in which the volume of the nitrogen is determined, also gave 13·7 per cent. The whole analysis, with the weighings, may easily be executed in an hour and a half by a single person. It is easy to see that this method applies to all inorganic nitrates and nitrites, whether hydrated or anhydrous, but that it cannot be employed in the case of organic or ammoniacal salts. In the analysis of inorganic nitrates or nitrites by Simpson's method, it is not necessary to use oxide of mercury to prevent the formation of deutoxide of nitrogen. In all such cases it will be found sufficient to mix the salt with pure metallic copper. In this manner the dimensions of the combustion-tube may be greatly diminished. It is also advantageous to pump out the air from the combustion-tube by a small hand air-pump before disengaging carbonic acid from the carbonate of manganese. By alternately pumping and filling the tube with carbonic acid, the air may be completely expelled before the combustion commences. It is also better to draw the tube out before a Bunsen's blowpipe, as it is difficult to make a cork and india-rubber connector perfectly tight. With a little practice the drawing out is easily effected even with the hardest combustion-tubes.

Estimation of Nitrogen by Evolution as Ammonia.

The substance is mixed with soda-lime, put into a combustion-tube and decomposed in the ordinary way, but instead of passing the resulting gases into hydrochloric or sulphuric acid, they are at once passed into a dilute solution of chloride of zinc. It is obvious that one equivalent of ammonia will form one equivalent of oxide of zinc, which only requires to be filtered, washed, dried, and ignited. From the weight of the ignited precipitate the quantity of nitrogen or ammonia is easily calculated, 40 of oxide of zinc being equal to 14 of nitrogen or 17 of ammonia. This process gives accurate results.

Solution of chloride of zinc is stated by Mr. Walker, to whom this process is due, to be preferable to other metallic solutions, for the following reasons:—Solutions of iron are difficult to preserve without undergoing decomposition. The precipitate formed with proto-salts of manganese is partially altered into peroxide upon ignition. Solutions of cobalt or nickel may answer, but they are not so easily obtained in a pure state as zinc. Oxide of copper is not perfectly precipitated by ammonia. A solution of

zinc can easily be prepared free from any impurities; it will keep for any length of time without alteration, and whether it be ammonia or carbonate of ammonium that is passed into the solution, the precipitate is ultimately obtained upon ignition as oxide of zinc. The solution should be dilute, specific gravity 1·025, and about 10 fluid ozs. should be taken for each analysis; for washing the precipitate water at about 150° F. should be used.

Detection of Nitric Acid.

The following test, proposed by Mr. Blunt, for the presence of nitrates in a drinking water is a little more delicate than the common one with ferrous sulphate; it depends on the reducing action exercised by sodium amalgam on nitric acid.

When a moderately concentrated solution of nitrate of potassium is poured over an amalgam of sodium containing about ½ per cent of the metal, there is no evolution of hydrogen, and on pouring off the supernatant fluid after some minutes, and applying the Nessler test, a considerable quantity of ammonia may be detected. A solution of pure nitrate of potassium, containing 1-50th grain of the salt, gives a just perceptible colouration with the Nessler test after standing over a ½ per cent amalgam for about twelve hours; 1-25th grain of the salt gives a marked reaction. Several attempts have been made to adapt the above test to the estimation of small quantities of nitric acid; they have at present, however, been unsuccessful, through the impossibility of pushing the reaction to completion; it is possible, however, that a system of comparative testing analogous to that at present adopted in the case of ammonia may lead to some results. As an example of the mode of applying the test qualitatively to a drinking water, the following account may be given of an actual experiment:—

To 2 ozs. of a water known to contain a trace of nitrates was added about 100 grains of a solution of hydrate of potassium, containing 1-12th of its weight of alkali; the whole was then evaporated nearly to dryness; thus any ammonia already existing in the water would be expelled. The residue was exhausted with distilled water which gave no reaction with the Nessler test, and the quantity of the solution made up to 200 grain measures, which were afterwards divided into two equal portions. One was at once tested with ferrous sulphate solution and sulphuric acid; a very faint brown colouration appeared at the point of junction of the layers of liquid, increasing considerably after a few hours.

The second portion was introduced into a carefully cleaned test-tube, with about 200 grains of ½ per cent sodium amalgam: the tube was lightly corked to check, as far as possible, diffusion of the ammonia formed, but not

so tightly as to prevent the egress of the hydrogen, which in dilute solutions of a nitrate is always evolved from the amalgam. The whole was left for about twelve hours; the liquid was then rinsed with successive portions of pure distilled water into a glass cylinder about 6 inches high and 1 inch wide, and the quantity was made up with distilled water to about 1000 grains. On adding about 15 grain measures of the Nessler test, a very strong colouration, accompanied by incipient precipitation, at once appeared. It is to be remarked that the liquid must always be decanted from the amalgam before applying the Nessler test, as the presence of nascent hydrogen appears to interfere with the action of the latter.

M. F. Bucherer gives a process which he states will detect 1-100,000th of a nitrate in aqueous solution. It is founded on the action of nitrous vapours on iodide of potassium; the potassium is oxidised by the oxygen of the nitrous vapours, which are thereby reduced to the state of binoxide, and iodine is set at liberty. For the test to be conclusive, any chlorine or bromine must have been separated from the liquid. The author places 8 or 10 grms. of the liquid to be tested in a tube 6 or 8 inches long, introduces a few copper turnings, and 3 or 4 drops of strong sulphuric acid. Then boil for a moment and nearly fill up the tube with water; now add a few drops of a solution of iodide of potassium. If the liquid contains any nitrate the iodine is set at liberty, and on adding a small quantity of disulphide of carbon and shaking vigorously, the sulphide will dissolve the iodine, and float on the surface of the liquid, taking a violet or deep red colour, according to the quantity of iodine displaced.

To detect free nitric acid operate as above, but omit the sulphuric acid. To detect a nitrite use the same method with the omission of the copper.

Estimation of Nitric Acid.

From the numerous methods of estimating nitric acid which have been published within the last few years, the following are selected as being the most convenient and trustworthy.

A. Estimation of Nitric Acid by the Oxidation of a Proto-salt of Iron.—This is commonly known as Pelouze's method. The weighed nitrate is boiled out of contact with air with a solution of protochloride of iron and an excess of hydrochloric acid. Under these conditions the nitric acid splits up on the one hand into oxygen, which converts the proto-salt of iron into a per-salt, and on the other into a lower oxide of nitrogen which escapes. The requirements of this process are, firstly, that the decomposition of the nitrate shall take place in an atmosphere of which oxygen does not form a part, and, secondly, that such decomposition shall be complete.

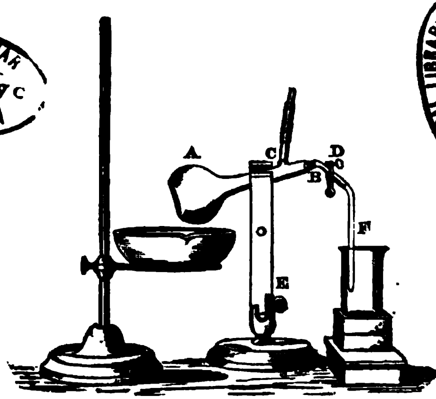
In the ordinary mode of conducting this process the operation takes

place in a retort, through which a current of hydrogen is passed. Attached to the stem of the retort is a U-tube, containing a little water, which serves as a lute to prevent access of air.

Mr. Holland has modified this arrangement so that the operation is conducted *in vacuo*, and at its termination the solution is boiled to expel the nitric oxide, thus avoiding the necessity of employing either hydrogen or carbonic acid.

In the accompanying sketch, A is a long-necked assay flask drawn off at B, so as to form a shoulder, over which is passed a piece of French india-rubber tube, D, about 6 centimetres long, the other end terminating in a glass tube, F, drawn off so as to leave only a small orifice. On the elastic connector, D, is placed a screw compression clamp. At C, a distance of 3 centimetres from the shoulder, is cemented with the blowpipe a piece of glass tube about 2 centimetres long, surmounted by one of French tube rather more than twice that length. The elastic tubes must be securely

FIG. 7.



attached to the glass by binding with wire. After binding, it is as well to turn the end of the connector back and smear the surface with fused caoutchouc, and then replace it. This device is recommended by Dr. Sprengel for securing an air-tight joint. The wooden clamp, E, gives support to the flask; the rest of the arrangement requires no explanation.

The analysis of a nitrate is conducted as follows:—A small funnel is inserted into the elastic tube at C, the clamp at D being for the time open; after the introduction of the solution followed by a little water, which washes all into the flask, the funnel is removed, and the former placed in the inclined position it occupies in the figure. The contents are now made

to boil so as to expel all air and reduce the volume of the fluid to about 4 or 5 c.c. When this point is reached, a piece of glass rod is inserted into the elastic tube at C, which causes the water vapour to find egress through F.

Into the small beaker is put 50 c.c., more or less, of a previously boiled solution of protosulphate of iron in hydrochloric acid. (The amount of iron already existing therein as a per-salt must be known).

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the caoutchouc connector slightly compressed with the first finger and thumb of the left hand. As the flask cools the solution of iron is drawn into it; when the whole has nearly receded the elastic tube is tightly compressed with the fingers, whilst the sides of the beakers are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than necessary or admit air. Whilst F is still full of water, the elastic connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion of the flask.

After heating at 100° C. for half an hour, the flask is removed from the water-bath and cautiously heated with a small flame, the fingers at the time resting on the elastic connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide through F, which should be below the surface of water in the beaker whilst these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled, and the solution of iron shows only the brown colour of the perchloride. At the completion of the operation the beaker is first removed, and then the lamp.

It now only remains to transfer the solution of iron to a suitable vessel, and determine the perchloride with chloride of tin in the usual way, or with subchloride of copper (see p. 72).

The process is easy of execution, and gives satisfactory results. The points requiring attention are that the apparatus should be capable of retaining a sufficiently perfect vacuum during the operation; this condition is fulfilled by the use of suitable elastic tube and clamps. What is known as French tubing serves the purpose well; its sides are thick, and its material free from metallic oxides.

It is advisable when making the digestion at 100° to place the flask in

cold water, which is afterwards raised to the boiling-point; if this be not done, but, on the other hand, the flask is heated at once, a violent bumping ensues, and portions of the liquid are projected into the tube at c.

B. Estimation of Nitric Acid when in the Free State.—Nitric acid dissolved in water is most easily estimated by acidimetric processes. It has been proposed to evaporate the acid liquid with a given weight of oxide of lead; but oxide of lead forms with nitric acid various insoluble basic combinations, which retain a certain quantity of water of 160°, and attract atmospheric carbonic acid. Oxide of lead may be advantageously replaced by baryta water and carbonate of barium.

C. Estimation of Nitric Acid when Combined with Heavy Metals.—The nitrates of metals precipitable by sulphuretted hydrogen being first decomposed by this reagent, the nitric acid can be estimated in the liquid by baryta, the excess of sulphuretted hydrogen being previously eliminated by sulphate of copper. Sulphide of barium does not well take the place of sulphuretted hydrogen; there is risk of the formation of hyposulphites, which might interfere with the estimation.

D. Estimation of Nitric Acid when Combined with any Base.—Nitric acid in combination may be estimated by distilling with dilute sulphuric acid, and determining the nitric acid in the distillate. Two litres of the solution are boiled down to about 200 c.c., and during evaporation pure permanganate of potassium is added (the object of which is to convert nitrites into nitrates), until a permanent pink colour is obtained. The concentrated liquid is filtered, pure sulphuric acid added, and distilled into a flask containing carbonate of barium suspended in water. The distillation is interrupted when sulphuric acid begins to go over. The contents of the receiver are filtered, and in the filtrate which contains nitrate and chloride of barium the barium is determined in the usual manner. The amount of chlorine being known from a separate experiment, all data are given for the calculation of the quantity of nitric acid present in the 2000 c.c. of water.

The error caused by the oxidation of ammonia to nitrous and nitric acid is inappreciable.

Instead of collecting the nitric acid in carbonate of barium, a standard caustic alkaline solution may be employed. A very good method consists in distilling nitrates with sulphuric acid diluted with twice its volume of water. The operation is conducted at a temperature not above 70° or 80° C. in a retort with the neck drawn out and bent, so that by means of an india-rubber tube it may be connected with a little receiver with three bulbs, containing a known volume of a standard solution of soda or potash. The distillation must be continued for three or four hours to obtain 1 or 2 grms. of nitrate. The distillation may be effected by a water-bath in a vacuum either by means of an air-pump, or by expelling the air from the apparatus

by boiling, and then closing hermetically. If the nitrate is mixed with chloride, a solution of sulphate of silver or moist oxide of silver is added previous to distillation.

E. Estimation of Nitric Acid by Fusion or Calcination.—Nitric acid may be estimated by difference in some salts decomposable by calcination, unless the production of a higher oxide of the base may occur. Nitric acid may be driven off by sulphuric acid, the weight of the sulphate being deducted from that of the nitrate.

Nitrates with strong bases are transformed into chlorides by calcination with chloride of ammonium.

Nitrates may also be decomposed by fusion with borax, or, better still, with bichromate of potassium. The crucible is weighed with the alkaline nitrate, heated, and melted sufficiently to melt the nitrate; bichromate of potassium is added after cooling (2·25 of bichromate for 1 nitrate); the whole is gently heated and weighed. The crucible is then gradually heated to dull red heat, and weighed after cooling. The difference gives the weight of nitric acid. Neither chlorides nor sulphates are decomposed under these conditions.

Estimation of Nitrites.

A. When a Considerable Quantity is Present.—In this case the following processes devised by Mr. Tichborne will be found very successful. The first process is based upon the reduction of chromic acid to chromic oxide by nitrous acid. If analysing a specimen of commercial nitrite of sodium, the mode of procedure is as follows:—If the sample contains carbonate of sodium, a weighed quantity, say 2 grms., is dissolved in a rather considerable quantity of water, and the carbonate present estimated by a standard solution of sulphuric acid, carefully avoiding an excess. To hit the exact point of saturation, soak a piece of good litmus-paper in the solution after the addition of each quantity of acid from the burette, and on drying it the exact state of the solution is perceived. A convenient indicator of the point of saturation in this case will be found in a solution of starch and iodide of potassium contained in a test-tube; one drop of the solution of nitrite added after each addition of acid will, when the carbonate is all decomposed, strike a blue shade on falling through the starch solution. After noting the amount of carbonate, the solution is in a fit position for the estimation of the nitrite; the remainder may practically be noted as nitrate. Three grammes of pure bichromate of potassium for every two grammes of nitrite taken are dissolved with a little water in a flask fitted with a well-ground stopper; an excess of sulphuric acid is then added, and the flask is placed in a vessel containing a mixture of sulphate of sodium and hydrochloric acid. The solution of the nitrite

may be placed also in the same freezing bath for a few minutes previously to being poured on the surface of the chromic acid without mixing; the stopper is then inserted, the flask taken out of the freezing mixture, inverted, and left to regain the ordinary temperature of the room; in the course of half an hour or an hour the flask will contain a mixture of chromic acid and chromic salt, the chromic oxide representing the nitrite in the sample.

In precipitating the chromic oxide a precaution is necessary. If there is any considerable excess of chromic acid left, which is generally the case, when examining commercial samples, the ordinary method of precipitating with ammonia would not do, as a brown precipitate of a peroxide of chromium not decomposable by ammonia is thrown down, although the substance is instantly decomposed, upon boiling, by a solution of potash into chromic oxide and chromic acid. It is therefore necessary to nearly neutralise with potash, and finish off with a few drops of ammonia, and boil until all trace of the latter substance is gone; but if accidentally too much potash is added, a few drops of chloride of ammonium and a boiling for a few minutes will rectify the mistake. If the manipulation has been correctly performed, it will be indicated by the colour. The dark brown colour instantly disappears on boiling, the precipitate obtaining the bright green of chromic oxide, whilst the solution becomes a bright yellow.

The chromic oxide is washed, but for accurate results it retains the chloride of potassium too tenaciously to ignite and weigh directly. It is better to re-dissolve the washed hydrated chromic oxide in dilute hydrochloric acid, and to re-precipitate with ammonia in the usual manner. This gives the most exact results; but there are quicker methods. Thus, the hydrated chromic oxide might be washed and converted into chromic acid by Chancel's method (by peroxide of lead) and estimated volumetrically.

Chromic oxide found $\times 1·354 =$ nitrite of sodium.

The second process is based upon the first, that both nitrites and nitrates of the alkalies are converted into chlorides, upon ignition with chloride of ammonium.

Pure nitrite of sodium gives 84·78 per cent of chloride of sodium, whilst nitrate of sodium only gives 68·82. From these data, it is therefore easy to calculate the percentage, as anything under 84·78 indicates the presence of nitrate.

It must be borne in mind that if the specimen contains carbonate, this would give the percentage of nitrite too high. As 100 parts of carbonate would give 110·37 parts of chloride of sodium after ignition, therefore it will be necessary to deduct an equivalent quantity of chloride of sodium from the results before calculating them. A weighed quantity of the nitrite is intimately mixed with powdered chloride of ammonium, and introduced

into a platinum crucible; a gentle heat is applied, until the whole of the excess of sal-ammoniac and other gaseous bodies are volatilised. The residue is dissolved in water, and the chloride of sodium estimated volumetrically with a silver solution.

After a deduction for any carbonate of sodium present, the calculation may be made thus:—

$$\frac{(NaCl - 68{\cdot}82) + 100}{15{\cdot}96} = x,$$

x being the percentage of nitrite of sodium. The chloride of sodium left, minus the percentage of nitrate, divided by the difference (15·96), will give the percentage of nitrite, or *vice versa*:—

$$\frac{(84{\cdot}78 - NaCl) + 100}{15{\cdot}96} = x,$$

x being in this case nitrate of sodium; nitrite of ammonium in solution is resolved on boiling into nitrogen and water.

B. When Minute Quantities only are Present.—Nitrites have the property of liberating iodine from an acidified solution of iodide of potassium. Dr. Angus Smith asserts that an amount of nitrous acid, so small as 1 in 3¼ millions of water, may easily be discovered in this manner. Mr. P. Holland has made use of this qualitative test for the purpose of quantitative estimation, the colouration imparted by the free iodine being taken as the measure of the nitrous acid present. For a "colorimetric" standard, solution of iodine in iodide of potassium is taken; about 4 grms. is dissolved in excess of iodide, and made up to the volume of a litre. In the next place, it is necessary to prepare a pure salt of nitrous acid; for this purpose, commercial nitrite of potassium is precipitated with nitrate of silver, the resultant silver salt washed by decantation, re-crystallised, and dried *in vacuo*.

To 0·3276 grm. of the silver salt, dissolved by heat in water, is added a slight excess of pure chloride of sodium, and the liquid, when cold, made up to the volume of 1000 c.c., therefore 10 c.c. = 1 mlgrm. of nitrous acid.

The iodine solution is "titrated" as follows:—A permanganate burette divided in 1-10ths of a c.c., and fitted with a float, is filled with it. Two narrow white glass jars are placed on a white slab; on each is marked the point at which a volume of 200 c.c. of water stands. Into one, A, is put an amount of the standard nitrite equal to 1 mlgrm. of HNO_2, together with 6 c.c. of iodide of potassium (1 to 10 of water), then distilled water nearly to the mark, and lastly dilute H_2SO_4. The whole is to be mixed and allowed to stand until the colour is fully developed; when that point is reached, the second jar, containing an amount of iodide of potassium and acid equal to that in A, is filled to within a short distance of the volume mark with water, and placed under the burette; the iodine solution is then

cautiously delivered into it, until the depth of colour is judged to be equal in intensity to that in A. The iodine solution should be of such a strength that 10 c.c. have a colouring power equal to that possessed by 1 mlgrm. of HNO_2 in the presence of iodide of potassium in a volume of 200 c.c. of water. It is unadvisable, when making the comparison, to add the standard nitrite from a burette to an acidified solution of iodide of potassium, for an obvious reason. It may, however, be suggested that a definite quantity of nitrite should be added together with iodide to the water in the jar, and lastly the acid. Such a method is tedious, in that it would be necessary to make several assays before attaining the desired shade.

The following determinations of nitrous acid have been made in this manner:—An amount equal to 1 mlgrm. was evaporated with a litre of spring water to the volume of 100 c.c., the residue was filtered into the cylinder, and the filter washed; when cold some iodide of potassium was added, then distilled water to within ¼ inch of the mark, and lastly dilute sulphuric acid. After thoroughly mixing, the contents of the cylinder were left undisturbed, for the colour to become fully developed; when that stage arrived it was found that 11·5 was the number of c.c. of iodine requisite to impart the same colour to an equal volume of water. Ten c.c. should only have been required; the excess, therefore, of 1·5 c.c. is the measure of the nitrous acid in the water employed.

The process is not suitable when the quantity of nitrous acid is large; whilst it ranges below and up to 1 mlgrm. corresponding results can be obtained.

Some precautions are necessary in certain cases. Sulphuretted hydrogen and sulphides must be removed if present; the former escapes during the evaporation of the water; the latter may be decomposed by a metallic oxide. Organic colouring matter can be precipited by means of chloride of calcium, carbonate of sodium, and a few drops of hydrate of potassium, as suggested by Dr. Frankland. Kaolin could perhaps be employed for the purpose.

CHAPTER XII.

IODINE, BROMINE, CHLORINE, FLUORINE (CYANOGEN).

IODINE.

Purification of Iodine by Sublimation.

IODINE should not leave any residue when exposed to a high temperature. Impure iodine may be purified by sublimation in the following manner:— Place it in a large watch-glass resting on a plain glass plate, and heat it on a sand-bath to 107° C. (the melting-point of iodine); a well polished beaker is inverted over the watch-glass, and in this the iodine condenses.

Assay of Commercial Iodine.

The methods generally adopted, based on the well-known reactions of sulphurous acid or hyposulphide of sodium, yield excellent results in experienced hands, but are attended with many sources of error, owing to the rapid alterations in the standard solutions. Mohr's method, based on the use of arsenite of sodium, is much more accurate, and with the modifications introdued by M. A. Bobierre, leaves little to be desired on the score of accuracy or speed.

Make a concentrated solution of iodide of potassium, which should remain unchanged for a certain series of experiments: this is to dissolve the iodine which is to be tested. The standard solution of arsenite of sodium is obtained by dissolving 4·95 grms. of arsenious acid with 14·5 grms. of crystallised carbonate of sodium, and diluting the aqueous liquid to 1 litre. This solution should decolourise an iodised liquid containing 12·688 grms. of iodine per litre. But supposing that the arsenious liquid may not have this reducing power, the test will be none the less exact, as at the time of performing it the relation of a given weight of pure iodine to the arsenite will also be determined. A somewhat concentrated solution of bicarbonate of sodium is also to be prepared.

The analysis is best effected in a small stoppered flask. Into this are put 10 c.c. of the arsenite of sodium, to which must be added 5 c.c. of alkaline bicarbonate solution; the whole then receives a further addition of about 4 c.c. of perfectly colourless benzol.

Weigh a certain quantity of pure iodine between two watch glasses; dissolve this in the concentrated solution of iodide of potassium prepared beforehand, and which must be of the same strength in all the various estimations which may be made; with this coloured solution fill a flask containing 100 c.c., shake it, and pour the contents into a graduated burette.

On allowing the iodised solution to fall into the arsenite drop by drop, and stirring it quickly, the brown colour will be seen to disappear instantaneously; but scarcely will all the arsenite have been changed to arseniate, when the addition of iodine will produce a double reaction; in the first place, the benzol will turn red; secondly, the aqueous liquid, which was perfectly colourless at the beginning of the operation, assumes a very sensible yellowish tinge; the significant character of this is the more surprising when we remember the very small quantity of iodine which causes it.

A second experiment is now to be performed upon the iodine to be estimated, and the same weight being used, its standard is at once shown, since the volume of solution requisite to destroy the alkaline arsenite is in inverse proportion to the quantity of real iodine to be determined.

Detection of Minute Quantities of Iodine.

1. Make a mixture of water, 100 grms., starch, 1 grm., nitrite of potassium, 1 grm.; boil this for five minutes; it will then keep for years without deterioration. When required for use, take 10 c.c., and add to it one drop of hydrochloric acid. Take a piece as large as a pin's head of the dry salt to be tested for iodine, place it in a clean porcelain capsule, and add a drop of the test fluid. When no iodine is present, no colouration ensues; but the least trace of iodine gives rise to the formation of a well-defined blue colour.

2. Carey Lea makes use of the oxidising properties of chromic acid to liberate iodine from its hydrogen and metallic combinations, and thereby bring about the starch reaction.

If, for example, we take an extremely dilute solution of iodide of potassium, such that the addition of nitric acid and starch produces no perceptible effect, the further addition of a single drop of very dilute solution of bichromate of potassium will instantly bring about the characteristic reaction. When hydrochloric acid is substituted for nitric, the effect of the bichromate is still more marked. The test has, then, the full delicacy at least of the chlorine test, with this great advantage, that an excess of the reagent does not prevent the reaction. As to the delicacy of this test, the following observations have been made:—With solutions of iodide of potassium up to 1-100,000th the precipitate is abundant, becoming less blue and more tawny as the dilution increases. Beyond this point the distinct-

ness rapidly falls off. The indications are observable at 1-400,000th. With a solution of 1-800,000th it is doubtful whether any effect is evident. The experiment can be made in two ways, according to the result desired.

In employing the reagent in the search for iodine, add the starch to the liquid to be tested, stir it up, add a drop of dilute solution of bichromate of potassium, enough to communicate a pale yellow colour, and finally add a few drops of hydrochloric acid. The test is then the production of the characteristic precipitate, or in case of great dilution, approaching to a half-millionth, merely the tawny shade given to the solution.

If a very great excess of acid is used, and too much bichromate taken, the starch may be made to reduce the bichromate. Even this, however, cannot deceive, for a bluish-green solution is thereby produced, whereas the indications of iodide are in the order of their strength—blue precipitate, tawny precipitate, tawny solution. Unless in the case of very exceptional dilution above spoken of, a well-marked blue precipitate is always obtained.

3. The method of estimating iodine by the hyposulphite process is best conducted as follows:—

Prepare a normal standard solution containing, for each litre of water, about 40 grms. of hyposulphite of sodium, so that 50 c.c. of this solution will completely decolourise 1 grm. of iodine.

Then take 10 c.c. of the iodised liquid to be tested, diluted with water if it be very concentrated or rich in iodine; then add carefully, after it has been acidulated with hydrochloric acid, some drops of hyponitric acid. When it becomes yellow, shake it with benzol or petroleum, which will immediately turn rose or violet. Separate the iodised benzol from the acid liquid, and repeat the operation until the solvent liquid ceases to become coloured.

Collect the iodised benzol resulting from these treatments, and wash it with distilled water, which will remove all traces of chlorated or bromated compounds without removing any appreciable quantity of iodine. Then, with constant stirring, add, by means of a burette, graduated to tenths of c.c., the standard hyposulphite liquid until all colour is destroyed; each cubic demi-centimetre of the normal liquid will correspond to one centigramme of iodine contained in the liquids assayed.

It is always necessary to desulphurise solutions containing sulphides, sulphites, or hyposulphites, by boiling them with nitric, sulphuric, or hydrochloric acid.

To ascertain the purity of commercial iodines, dissolve about 50 centigrammes in diluted alcohol, and operate as above.

To ascertain the quantity of iodine in dry or wet sea plants, cut them into small pieces; place them in a porcelain capsule and cover them with alcohol; set fire to the alcohol, carefully stir the mass with a glass rod, and

the carbon will be obtained without loss of iodine; then well wash the latter, and act on the solution as above described.

Estimation of Iodine in Organic Liquids.

1. There are met with in commerce mother-liquors which are utilised for the manufacture of iodine, and which contain, besides this metalloid, sensible quantities of alkaline arseniates and arsenites, as well as organic matter. These liquids occur in the manufacture of aniline colours, and their value depends upon the amount of iodine they contain. The following is the best process to adopt for estimating this:—10 grms. of liquid are treated with 2 grms. of concentrated solution of caustic potash; the mixture is then evaporated to dryness under a chimney with a good draft, or in the open air, on account of the cacodylic products occasionally evolved; it is ultimately ignited. The aqueous solution of the residue is diluted with water and treated by a mixture of sulphuric and hyponitric acids. The iodine is separated by agitating with sulphide of carbon; and this sulphide of carbon solution agitated with water until the washings no longer affect litmus paper; when this is attained, a titration of the iodine present is made with hyposulphite or arsenite of sodium.

2. To estimate the iodine contained in organic hydriodates, M. Kraut proposes that their solution be digested for some time with a known weight of recently precipitated chloride of silver; the chlorine is replaced by iodine, and from the increase in weight of the chloride of silver, the amount of iodine may be calculated. This method has the advantage of not altering the substance beyond removing its iodine, which is replaced by chlorine.

BROMINE.

Detection of Bromine.

The best solvent for bromine just displaced by chlorine is disulphide of carbon, a substance long used in France for detecting iodine. M. Fresenius, who has verified this fact with his usual care, insists on the necessity of avoiding excess of chlorine, and of employing disulphide of carbon free from sulphurous and sulphuric acid.

His preference for disulphide of carbon over ether and chloroform is founded on a series of direct experiments with standard solutions containing various proportions of bromides. Solutions containing only 1-30,000th of bromine in the state of bromide of potassium, when treated with the requisite quantity of chlorine, do not communicate the least colour to ether or chloroform, while disulphide of carbon acquires a decided yellow tint. Moreover, being heavier than water, it sinks to the bottom of the liquid with the bromine it has dissolved, and there remains.

If the bromide is accompanied by an iodide, the iodine must be previously eliminated by adding a little hyponitric acid and a drop of disulphide of carbon, which takes away the displaced iodine. After this the separation of the bromide may be proceeded with.

Estimation of Bromine and Iodine in the Presence of Chlorine.

1. This process is of special use for the assay of mother-liquors from saltpetre and kelp. A measured quantity of the liquor is introduced into a long tube with 20 alkalimeter measures of disulphide of carbon; and nitrous-sulphuric acid (prepared by passing nitrous acid through sulphuric acid) is added, drop by drop, till iodine ceases to be liberated. The tube is inverted several times after the addition of each drop of acid, in order that the iodine may at once be dissolved by the disulphide of carbon, to which it gives a violet colour, varying in intensity with the amount of iodine in solution. The quantity of the iodine is estimated by comparing the degree of the colour with that which results when a standard solution of iodide of potassium is used in the same way. The delicacy of the reaction is such, that 0·01 gr. will communicate a distinct rose tint to the disulphide of carbon. When the amount of iodine exceeds 0·2 gr. of iodine in the quantity operated on, a difficulty occurs, as the violet colour becomes so deep that the various shades cannot be distinguished with accuracy. When all the iodine is separated by the disulphide of carbon, the solution containing the bromine is introduced into another tube, and the bromine is liberated by chlorine-water in the usual way, and taken up by a fresh quantity of disulphide of carbon. In this case, an orange colour is the result, and the amount of bromine may be estimated by comparing the colour with that resulting when a solution of bromide of potassium is used of known strength.

2. Colour tests being always liable to much uncertainty in their indications if any great accuracy is desired, the following process may be found preferable. It is devised by Mr. Tatlock, and is based upon the wide difference between the equivalents of iodine, bromine, and chlorine. The mode of procedure depends upon the displacement of iodine by bromine, and of iodine and bromine by chlorine.

The solution containing the iodide, bromide, and chloride, preferably in combination with an alkali metal, is divided into three equal portions, or, at any rate, three equal portions of it are drawn off. To the one, solution of nitrate of silver is added in excess, to precipitate the whole of the iodine, bromine, and chlorine. The fluid is then feebly acidified with pure nitric acid, warmed, and agitated till the precipitate settles. This is collected on a small weighed filter, washed with hot water, dried as far as possible at 100° C., removed from the filter, dried perfectly by heating to incipient

fusion, and weighed, the weight of the small portion adhering to the filter being added, and the weight of the whole noted as—

$$AgI + AgBr + AgCl.$$

Another portion of the solution is transferred to a small basin, and a quantity of pure bromine-water added. The mixture is then carefully evaporated on an open water-bath, more bromine-water being added from time to time, till the escaping vapours no longer turn starch-paper blue on a fresh addition—showing that all the liberated iodine has escaped. To ensure excess, a little more bromine-water is added, and the solution evaporated to complete dryness. The dry residue is then drenched with water, and the result heated till again dry; this operation is repeated two or three times, to ensure the complete expulsion of any hydrobromic acid that may have been present in the bromine-water. The residue, which now consists solely of alkaline bromide and chloride, is dissolved in water, nitrate of silver added in excess, the solution acidified, and the precipitate collected and weighed in the usual way. It is noted as—

$$AgBr + AgBr + AgCl.$$

The last portion of the solution is brought into a small basin, and a quantity of strong chlorine-water added, to effect the liberation of the iodine and bromine. The mixture is then evaporated till all colour is gone, and some more chlorine-water added. If the solution remains colourless, the whole of the iodine and bromine has been expelled, and the alkali metal will exist entirely as chloride. The solution is then brought completely to dryness, after which it is evaporated with a few drops of water two or three times, to expel any hydrochloric or hydrobromic acid. The dry residue is dissolved in water, the solution acidified with pure nitric acid, nitrate of silver added in excess as before, and the chloride of silver collected as usual. Its weight is noted as—

$$AgCl + AgCl + AgCl.$$

It is obvious that we have now data from which we can calculate the amounts of iodine, bromine, and chlorine present; for, as the equivalent of bromine is less than that of iodine, in the proportion of 80 to 127, the second precipitate, in which the iodine is replaced by bromine, must weigh proportionately less than the first; and, as the equivalent of chlorine is less than that of either iodine or bromine, in the ratio of 35·5 to 127 in the one case, and to 80 in the other, the last precipitate must weigh still less than the second, and we can thus, from the observed differences, deduce the exact quantities of the three elements present.

Example :—

1. $AgI + AgBr + AgCl$	weighed	15·57
2. $AgBr + AgBr + AgCl$	,,	14·69
3. $AgCl + AgCl + AgCl$	,,	12·20

Then—

I.		II.		Observed difference.
15·57	−	14·69	=	0·88

Loss for 1 equiv. I.		Observed loss.		1 equiv. I.		I present.
47	:	0·88	::	127	:	2·378

I.		III.		Observed difference.
15·57	−	12·20	=	3·37

But, as a portion of this loss is caused by the replacement of iodine by chlorine, namely,—

Equiv. of I.		Loss in replacing 1 equiv. I by Cl.		I found.		Loss accounted for by I present.
127	:	91·5	::	2·378	:	1·713

Observed loss.		Loss accounted for by I present.		Difference for Br.
3·37	−	1·713	=	1·657

Loss for 1 equiv. Br.		Observed loss on account of Br.		1 equiv. Br.		Br found.
44·5	:	1·657	::	80	:	2·978

Then, as the proportion of iodine and bromine are already known, it will be an easy matter to calculate them to iodide and bromide of silver, and deduct their weight from precipitate 1, calculating the remainder (chloride of silver) to chlorine thus:—

I.		AgI.		I present.		AgI.
127	:	235	::	2·378	:	4·400

And—

Br.		AgBr.		Br present.		AgBr.
80	:	188	::	2·978	:	6·998

Then—

AgI	4·400
AgBr	6·998
	11·398

Then—

$$15·57 - 11·398 = 4·172$$

Then—

AgCl.		Cl.		AgCl.		Cl.
143·5	:	35·5	::	4·172	:	1·032

There were, therefore, present in the solution—

Iodine	2·378
Bromine	2·978
Chlorine	1·032

The bromine-water may be easily obtained free from chlorine by distilling bromide of potassium in solution with less bichromate of potassium than is necessary to expel the whole of the bromine, using, of course, a little hydrochloric acid.

Application of the Foregoing Method to the Analysis of Kelp.—It is quite obvious that this process cannot be directly applied to substances containing iodine, bromine, and chlorine, in very different proportions, and consequently it cannot be used for the estimation of these elements in kelp immediately. The following method of treatment will be found to equalise as nearly as necessary the proportions of the three:—

2000 grs. of the kelp are digested in hot water, the solution allowed to settle, and the clear liquor filtered. The residue is boiled two or three times with water, the fluid being filtered in each case, and the residue finally brought on a filter and washed with boiling water. The filtrates and washings are neutralised as nearly as possible with hydrochloric acid, and chlorine gas passed into the solution till the latter becomes of a distinct orange colour, due to the liberation of iodine and bromine.

The fluid is then shaken up with about one-fourth of its bulk of disulphide of carbon, which takes up the liberated iodine and bromine, and carries them in solution to the bottom of the vessel, provided the sp. gr. of the kelp solution be not higher than that of the disulphide of carbon. When this is not the case, the solution of kelp may be diluted till the disulphide of carbon sinks.

The bottom fluid, containing the iodine and bromine, is then drawn off by a fine syphon, and shaken up with an equal volume of water and some zinc-filings. The solution is soon decolourised, on account of the formation of zinc iodide and zinc bromide, which pass into the water; and we have thus an aqueous solution of the two latter salts above, and colourless disulphide of carbon at the bottom. The latter is drawn off by a syphon, and restored to the kelp solution, to which some more chlorine-water is added; and, if a further quantity of iodine and bromine be liberated, the above operations are repeated till the liquor is quite exhausted.

It only now remains to evaporate the solution of zinc salts, divide into three equal portions, and determine iodine, bromine, and chlorine, as before described.

Detection of Bromides in the Presence of Chlorides.

When chloride of gold is added to a faintly acid solution of an alkaline bromide, a colouration is produced ranging from dark orange-red to light straw-colour according to the strength of the solution. Iodides must not be present; chlorides, however, do not interfere. The best mode of proceeding is as follows:—Remove the iodides if present, by means of palladium,

and after getting rid of excess of palladium by sulphuretted hydrogen, concentrate the solution to about 25 c.c. Select two test-tubes of the same size and shape and colour of glass; into one pour the solution suspected to contain bromine, and into the other pour pure water containing a trace of chloride of potassium. Add to each tube one drop of hydrochloric acid, and one drop of chloride of gold solution. On now comparing the two tubes, particularly in the direction of the long axes, a yellow colour will be observed in the tube containing the bromide, which will be rendered very manifest by comparison with the other tube.

The mixed chloride and bromide should be brought to the state of alkaline salts if necessary, by precipitating with nitrate of silver, thoroughly washing and fusing with carbonate of *potassium*. If carbonate of sodium is used for this purpose the subsequent reaction with the gold test is not so decided.

Detection of Chloride in Bromide of Potassium.

The bromide to be examined is first tested for iodine. For this purpose a small quantity of the salt is dissolved in water in a test-tube, and an equal volume of disulphide of carbon added. Upon the addition of a few drops of bromine-water, the disulphide of carbon becomes coloured violet, under the influence of iodine, if this be present. When the test shows the presence of iodine, it is necessary to remove the whole of this element from the sample. This is effected by dissolving about 10 grms. of the salt in distilled water, adding bromine water until violet vapours are no longer visible upon boiling, and then testing for iodine in the manner first described. Afterwards the solution is evaporated to dryness to remove the excess of bromine, and thus is obtained a bromide of potassium free from iodide, but which may contain chloride.

The remainder of the process depends upon the fact, that a given weight of chloride of potassium requires, for complete precipitation, a much greater amount of a standard solution of nitrate of silver than the same weight of bromide of potassium. While the bromide for the complete precipitation of 1 grm. requires 1·428 grms. of nitrate of silver, 1 grm. of the chloride requires 2·278 grms. A standard solution of nitrate of silver is first prepared by dissolving 10 grms. of the pure salt in a litre of water, each 1-10th c.c. corresponding to 1 milligramme of nitrate of silver. 1 grm. of the bromide to be examined, freed as above from iodine, is dissolved in 100 c.c. of distilled water; 10 c.c. of this solution, representing 0·1 grm. of bromide of potassium, would require, if pure, 14·2 c.c. of the silver solution; chloride of potassium would require 22·7 c.c.

M. Baudrimont has proposed a method of making the final reaction more delicate, by adding a few drops of solution of chromate of potassium to

the bromide examined; the nitrate of silver added at first combines with the whole of the bromine and chlorine in preference, and the complete precipitation is marked by the production of the red precipitate of chromate of silver. It is obvious that the bromide contains more or less chloride, according as the number of burette divisions (divided into 1-10th c.c.) of the silver salt required exceeds 142. With a salt containing one-tenth of its weight of chloride of potassium 151 divisions are required, and with a mixture of equal weights of chloride and bromide, 185.

The same method may be employed to recognise the degree of purity of several compounds. Operating as before—that is to say, dissolving 1 grm. of the material to be examined in 100 c.c. of distilled water, and taking 10 c.c. of the solution—the following numbers of 1-10th c.c. divisions required will show the purity for at least a considerable number of salts:—102 for pure iodide of potassium, 257 for cyanide of potassium, 246 for dry carbonate of potassium, 290 for chloride of sodium, 119 for carbonate of sodium + 10 equivalents of water, 47 for phosphate of sodium + 24 equivalents of water, and 54 for arseniate of sodium + 14 equivalents of water.

Detection of Iodine in Bromide of Potassium.

When bromide of potassium is suspected to be adulterated, or mixed with iodide of potassium, place a few grains of the salt in question on paper previously impregnated with starch paste, moisten it, and admit a small quantity of chlorine gas, whereby the iodine is set free and the paper coloured blue.

A better test is the use of bromine-water added to the salt after it has been placed in benzol; if the latter becomes red-coloured, iodine is present.

CHLORINE.

Estimation of Chlorine in Bleaching Powder.

A. The commercial estimation of bleaching powder only extends to the estimation of the hypochlorite contained therein; the result being, however, calculated as so much per cent of "available chlorine." Of the numerous methods proposed for the determination of the hypochlorite, the one usually employed in the trade is that depending on the amount of ferrous salt oxidised by a given weight of bleaching powder. It frequently happens, however, that instead of a perfectly pure ferrous salt (such as the ammonio-sulphate precipitated by alcohol), the ordinary protosulphate of iron of the druggists is used, discoloured crystals being of course rejected; this substance is, however, rarely pure, and hence errors are frequently introduced, less chlorine being required to peroxidise a given weight of

impure than of pure substance. Again, some analysts neglect to add an acid to the ferrous solution used, and hence the precipitated ferric hydrate is liable to carry down perceptible quantities of ferrous hydrate, again making the apparent amount of chlorine required less than that really requisite. When acid is added, an error is liable to be introduced by the peroxidation of part of the iron by chlorine compounds derived from chlorate that may be present; direct experiments have shown that acid ferrous solutions are perceptibly oxidised by the presence of chlorate in small quantities in the course of a very few minutes, even at the ordinary temperature, although the peroxidation due to the whole of the chlorate is not manifest until after standing some time at 20° C., or till after heating to ebullition. Lastly, the equivalent of chlorine is frequently taken to be 36 instead of 35·46 (Stas). All these sources of error tend to make the percentage of chlorine found higher than that really present; accordingly it frequently happens that analyses of the same sample by different analysts differ by 1, 2, or 3 per cents of available chlorine; this error becomes of serious importance, it frequently happening that the analysts employed by the seller and purchaser differ in their reports, thus causing much annoyance, and possibly the rejection of the goods as not being of contract strength.

As regards the error introduced by the presence of chlorate in the sample analysed, Mr. C. R. A. Wright has made many careful experiments on the subject which have yielded the following results:—

1. Acid ferrous solutions are peroxidised by addition of a chlorate, at a rate depending on the strength of the solutions, the amount of free acid, and the temperature, the reaction taking place completely after heating to ebullition for a minute, and almost as completely after standing for upwards of half an hour at 20° C., time being, however, required for any temperature short of ebullition.

2. Acid solutions of arsenious acid, where a large excess of free acid is present, are scarcely affected by chlorate at 20° C., until after standing some hours; the reaction ensues completely on heating to ebullition for a minute, and completely in a few minutes' heating on a water-bath.

3. Alkaline solutions of arsenious acid (containing carbonate of sodium and free carbonic acid) are wholly unaffected by chlorate, either cold or boiling, even after several hours.

4. Acid solutions of iodide of potassium (free from iodate). Iodine begins to separate even at 20° C. in a very few moments on addition of very little chlorate, and after some time much separates. Heated to 100° on the water-bath, the whole of the chlorate becomes completely decomposed, after five minutes, in presence of sufficient free acid.

5. Alkaline solutions of iodide of potassium are unaffected by chlorates even on long standing or long boiling.

Where the hypochlorite contained in a sample of bleaching powder, which may also contain chlorate, is to be determined, the only safe and convenient method is that of Penot, *i. e.*, by the use of an alkaline solution of arsenious acid. When the chlorate likewise is to be determined, it may be expeditiously done by heating the sample with a known quantity of the same arsenite solution, and addition of hydrochloric acid; from the difference between the quantities of arsenite peroxidised in the two instances the chlorate is readily known. Mr. Wright has found the bleaching powder of commerce to contain several per cents of chlorate of calcium, even when newly made; in older samples the chlorate has been occasionally found to represent as much as 10 per cent of available chlorine, or fully one-fourth of the amount originally present; thus indicating over-heating either in the process of manufacture or subsequently.

B. Two grms. of the bleaching powder to be tested are well mixed with water, and the fluid so obtained mixed with a solution of protochloride of iron freshly made by dissolving 0·6 grm. of pure iron wire in pure hydrochloric acid. Pure hydrochloric acid in excess is next added, and the fluid boiled in a flask, after previous addition of a piece of rather thick, perfectly clean, and polished sheet copper, of a weight of about 4 grms. The boiling is continued until the colour of the fluid, at first darkish, has become bright green; the copper is then removed from the flask, washed with distilled water, dried, and weighed. A loss in the weight of copper of 63·4 parts ($=2Cu$), is equal to 35·5 parts of chlorine in the bleaching powder. This method is based on the fact that, under the conditions described, the chlorine of the bleaching powder first changes the protochloride of iron into perchloride, which in its turn is again reduced to protochloride by the metallic copper, whereby some of the latter becomes dissolved; every 2 equivalents of copper dissolved in this way is equivalent to 1 equivalent of chlorine in the bleaching powder.

Detection of Arsenic in Hydrochloric Acid.

Take a thoroughly clean and dry test-tube, of not too narrow a bore; put into it as much pure protochloride of tin as can be placed on the point of a knife; next add from 4 to 6 c.c. of the hydrochloric acid to be tested; add, after this, gradually from 2 to 3 c.c. of pure concentrated sulphuric acid, taking care to move the test-tube very gently. If a white precipitate ensues, the addition of a few drops of the hydrochloric acid will be required to restore the liquid to perfect limpidity. If no arsenic is present, the liquid remains clear and colourless, even after standing for a time; but, if even a trace of arsenic is present, the fluid becomes at first yellowish, next brownish coloured, and at last the metallic arsenic is deposited as a deep greyish-brown flocculent substance. Even with only 1-500,000th part of

arsenious acid a colouration ensues. It is essential that when the sulphuric acid is added the liquid should become hot; if, therefore, that acid is too dilute to cause heating, the test-tube and contents should be warmed over a spirit flame.

Purification of Hydrochloric Acid from Arsenic.

1. *Preparation of Weak Acid.*—In the preparation of weak acid it is only necessary to boil the commercial arseniferous acid in a flat-bottomed dish until the acid is reduced to two-thirds its original volume. By allowing the hydrochloric gas to escape without collecting it, all the arsenic is taken with it in the form of terchloride, and the liquid remaining in the dish is no longer arseniferous; 8 litres of commercial acid, treated in this way, furnish in less than three hours 2 litres of weak acid free from asenic.

2. *Preparation of Fuming Acid.*—Into a flat-bottomed vessel of 6 litres capacity, first pour 3 litres of arseniferous acid, and add 0·3 gr. of powdered chlorate of potassium (0·1 gr. per litre). Then adapt to the mouth of the flask a cork pierced with two holes, into one of which fit a straight and strong safety tube; and into the other a larger tube, of the diameter used in organic analyses, 0·5 m. long, and serving, so to speak, as a vertical elongation. This lengthened tube should be very little tapered at its lower part; fill it with about 100 grms. of red copper turnings well beaten down to within 0·07 m. of its upper orifice, and then fill almost up with asbestos or broken glass. Pass the greater part of this tube through the neck of the flask, so that as much as possible of the surface may be heated by the hydrochloric vapour. Then furnish the upper part of the elongated tube with a tube to carry the gas into a receiver. In traversing the column of copper the acid gas is deprived of its chlorine, and arrives in a pure state in the water destined to dissolve it. The mode of operation is very easily comprehended. By boiling the acid the transformation of the chloride of arsenic into fixed arsenic acid is completed by the decomposition of chlorate of potassium; the excess of chlorine is taken with the moist hydrochloric gas into the copper, which most readily absorbs it, in preference to the acid, for which its affinity is much less. The chloride of copper returns to the flask in the form of a solution, while the gaseous hydrochloric acid condenses in the distilled water. But as it is important that there should always be, in the boiling acid, a slight excess of chlorine, to prevent the reduction of the arsenic acid, a constant current of hydrochloric acid, to each litre of which 1 grm. of chlorate of potassium has been added, should arrive through the safety tube (which should not dip more than from 3 to 5 c.c. into the liquid) so as always to maintain a small excess of chlorine, and at the same time to replenish the flask with hydrochloric acid to be purified. Generally the proportion of liquid acid thus added should

be greater than is required for distillation, otherwise there might be an insufficiency of chlorine. When the experiment has been successfully performed the hydrochloric acid contains neither arsenic nor chlorine.

By this apparatus pure hydrochloric acid may be constantly obtained without any sensible loss of acid, and the process may then be applied commercially.

3. Into the crude acid to be purified pass a current of sulphuretted hydrogen until all the arsenic is precipitated. Separate the sulphide of arsenic either by subsidence and decantation, or by filtering it through a funnel packed with amianthus. Remove the excess of sulphuretted hydrogen from the filtered liquid by addition of a concentrated solution of sesquichloride of iron, which destroys the sulphuretted hydrogen, being reduced to protochloride. Finally, rectify the acid from fixed matters.

See also the chapter on Arsenic, p. 260.

Valuation of Chlorate of Potassium.

After having proved the absence of heavy metals, those of the alkaline earths, and sodium, a certain quantity of the chlorate to be valued is dissolved in water. Some dilute sulphuric acid is then added to the solution, and a piece of zinc is placed in the mixture. The nascent hydrogen immediately transforms the dilute chloric acid into hydrochloric acid. In about half an hour the undissolved zinc is withdrawn from the liquor, the sulphuric acid is precipitated by nitrate of barium, and the zinc and excess of barium by means of carbonate of sodium. The hydrochloric acid in the filtered solution is then determined volumetrically by a standard solution of nitrate of silver. A convenient solution is made by dissolving 1·387 grms. of nitrate of silver in a litre of water; each c.c. of which solution will correspond to 1 milligramme of chlorate of potassium.

If the chlorate contains chloride, this chlorine is first precipitated by nitrate of silver, any excess of silver being removed from the filtered solution by sulphuretted hydrogen. The liquor filtered from the sulphide of silver may then be treated with zinc and sulphuric acid, as described above.

FLUORINE.

Detection of Fluorine in Water.

Treat the solid residue of a large quantity of the water with an excess of concentrated sulphuric acid, and pass the gaseous products into slightly ammoniacal water. If fluorine were present in the water, some gelatinous silica is precipitated in the liquid, resulting from the decomposition of the fluoride of silicon which was disengaged from the residue.

Estimation of Fluorine.

1. For estimating fluorine in combinations easily attacked by sulphuric acid proceed as follows:—Cover the platinum capsule in which the decomposition takes place with a funnel, resting with the capsule on a platinum basin, on which it is fastened with wet plaster; ascertain the weight of the funnel and the composition of the glass of which it is made. Heat the whole until most of the sulphuric acid has been expelled; then raise the funnel, wash it carefully, dry and weigh it; the decrease in its weight is owing to a portion of the glass having been attacked; and as its composition was first ascertained, the weight of silica which has been attacked may be calculated from the decrease in weight, and, consequently, the quantity of hydrofluoric acid which has been disengaged. This method has given very satisfactory results with triplite of Limoges, and with zivieselite, and other analogous phosphates of Schlaggenwald. With fluoride of calcium and cryolite too little fluorine is found, because the decomposition of these minerals is complete only when the mixture is properly shaken, which is difficult with the apparatus described above. The same funnel may be used many times, and is even better after it has been corroded.

If the substance to be analysed contains silica, the quantity must be ascertained and added to that of the glass attacked, to obtain the weight of fluorine.

2. Place the substance to be analysed in a rather deep platinum crucible, and cover it with three or four times its weight of silica; add a few drops of sulphuric acid, and heat gently for half-an-hour; then gradually increase the heat until most of the sulphuric acid is expelled. Then treat the whole with hydrochloric acid, add some water, and leave it to deposit; collect the deposit, calcine, and weigh it, and the loss of silica will indicate the amount of fluorine contained in the substance analysed (38 of fluorine correspond to 30 of silica).

The qualitative search for fluorine in substances free from silica is easily made, with small quantities of matter, in a platinum crucible furnished with a lid with a small circular hole pierced in the centre, above which a disc of glass is placed.

For the detection and estimation of fluorine in apatite, see p. 36.

CYANOGEN.

Detection of Minute Traces of Hydrocyanic Acid.

Good filtering paper is thoroughly soaked in tincture of guaiacum. After drying, it is moistened with water containing in solution 0·25 per cent of

sulphate of copper; this paper becomes coloured blue as soon as it is placed in contact even with very minute quantities of hydrocyanic acid.

Test paper prepared with a solution of iodide of potassium and starch solution will also, when previously moistened with the above-named solution of copper, become blue when placed in contact with small quantities of hydrocyanic acid, otherwise not readily perceptible.

CHAPTER XIII.

CARBON, BORON, SILICON.

CARBON.

Assay of Animal Charcoal.

THE points of greatest importance in an analysis of animal charcoal are the carbon, the carbonates, and the iron; the decolouriser, the neutraliser, and the destroyer. Under certain circumstances sulphates may be included, and in the case of unused charcoal the salts soluble in water should also be carefully estimated. The amount of phosphates is comparatively unimportant. The following is the process recommended by Dr. Wallace; it has frequently been verified during the author's work on beet-root sugar and the chemistry of sugar refining.*

Carbon.—Five grms. of animal charcoal are dried at 220° F., in a hot air-bath or paraffin-bath; the loss of weight gives the moisture, which, subtracted from the loss by calcination, furnishes the proportion of carbon.

Carbonate of Lime.—This can be quickly and accurately estimated by processes given in subsequent pages.

Iron.—After some little practice the iron can be safely estimated by Penny's process, using a very dilute solution of bichromate. The iron is always in a state of protoxide, faint traces of peroxide excepted, owing to the reducing action of the carbon in the re-burning.

Soluble Salts.—50 grms. of animal black are weighed and thrown into a little stoppered flask containing about 50 c.c. of distilled water: this is well shaken for a few minutes, and then filtered. The insoluble residue is re-digested in a fresh quantity of water; and this is repeated several times, so as to eliminate the whole of the soluble salts. The filtered liquid is evaporated over the sand-bath in a little porcelain capsule; the dry residue is weighed, and its weight gives the proportion of soluble salts. These salts consist of alkaline chlorides, sulphates, and carbonates; they also contain traces of sulphate and sulphide of calcium.

* "The Manufacture of Beet-Root Sugar in England and Ireland," by William Crookes. London: Longmans and Co., 1870.

Estimation of the Decolourising Power of Animal Charcoal.— In these estimations the object is to carry out the operation in such a manner as to obtain, as nearly as possible, the same results on the small scale in the laboratory as in the manufacturing operations; and it is because many little precautionary measures which tend towards the attainment of that equality are usually omitted in the laboratory, that such conflicting and apparently inexplicable results are recorded.

Mr. Arnot gives the following precautions to be observed so as to obtain trustworthy results:—

1. It must be decided what the results are to express; whether the relative decolourative power of equal bulks or equal weights of the charcoals, irrespective of size and proportion of grain, of the chars uniformly freed from dust, say by a fifty-mesh sieve; or of equal weights of equal grains.

2. According as either of these alternatives is decided upon, the various samples must be thoroughly and intimately mixed, and, if necessary, brought to an uniform dryness and temperature. It is always safest to have them thoroughly dry, and at a temperature of the surrounding air.

3. The various samples are next to be filled into glass tubes (tin may be used, but they preclude observations of a very important kind) provided with perforated false bottoms, covered with layers of cloth, and with taps capable of being accurately regulated. The tubes ought to be about 2 inches wide and 2 feet long, as nearly of the same diameter as possible. The best method of filling them is by passing the charcoal through a funnel, keeping the spout of the funnel moving constantly in a circular direction, so as to have the large and small grains equally diffused throughout. To allow the charcoal to run down either at one side, or, to a less degree, in the middle, is to cause to a certainty a separation of the larger grains from the smaller, and thus to create channels through which the liquor has too easy access.

4. See that no one tube is touched or shaken more than the others, after the charcoal has been filled in.

5. Sufficient brown sugar liquor, of, say, 24° B., must be prepared, either by diluting raw filtered liquor from the sugar-house to that gravity, or by dissolving as much of an average quality of raw material as will make sufficient liquor for the whole experiment. In the case of preparing it on the small scale, albumen must be liberally used, and the liquor passed through paper filters—coarse French paper answers best. The albumen should not be added till all the sugar has been dissolved, and the temperature at, say, 160° F. An equal quantity of the prepared liquor, as nearly 180° F. as possible, must now be poured uniformly upon the charcoal in each tube.

The rapidity with which the liquor passes through the charcoal in each case may be noted. Care must be taken to have the top of the charcoal always covered with liquor, and the taps below open. As soon as the liquor begins to drop at the taps they are closed.

6. The tubes being fully charged with liquor (there should be as much left on the tops of the charcoal as will serve to force out the liquor in the charcoal), they are put into a cistern of water at 140° F., the water in which will rise to about 1 inch from the mouths of the tubes; the time is noted, and the cisterns, which ought to be felted, covered.

7. At the end of not less than one hour (longer than one hour is sometimes advantageous, particularly if the raw liquor was very brown), the tubes are withdrawn, placed in their stand, and about 2 ounces of liquor run off each; this may be rejected, as the portion between the false bottom and taps is often turbid, and in addition has not been in contact with the charcoal for a sufficient length of time. The remainder of the liquor, *i.e.*, so much as has actually been in contact with the charcoal, may now be run off in three successive quantities for comparison. The results may be compared with any set of standard colours, and recorded accordingly.

8. If these results are not sufficiently conclusive, a further quantity of raw liquor may be run on each tube, and the whole transferred as before to the water-bath, which, if felted, will still be hot enough. The second quantity of liquor will be run off with the same precautions as the first, and the results will show the relative *persistency* of the charcoal under trial.

If the taps are large the liquor will be likely to run off too rapidly, and, in that case, they had better be partially and uniformly closed. If it is found that the liquor runs through one sample particularly slow, and through another particularly fast, it is quite admissible to assist the one by suction, and to check the other by closing the taps, but this should not be done unless in extreme cases, and the fact of having so assisted or retarded the process should always be noted.

It is scarcely necessary to mention the several points wherein the foregoing differs from the course usually pursued in testing charcoal, and yet it may be useful briefly to indicate some of these. Too little care is usually bestowed upon the selection and preparation of the samples. The tubes are, as a rule, too small: the charcoal cannot be run so uniformly into small tubes as large ones. The samples once charged with liquor are not usually kept warm: it is essential that they should. Some charcoals act powerfully at low temperatures, while others require a considerable amount of heat to bring out their maximum decolourative power; care must, however, be taken that the temperature employed does not exceed that attained on the large scale in the refining process. The fact just noted does not

seem to have been much investigated; it is worthy of careful consideration, not only on the part of experimentalists, but also by the practical refiner. One sample of charcoal, known to be of very inferior decolourative power on the working scale, persistently gave results, by the usual method of testing in the laboratory, equal to the very finest charcoal obtainable, but when kept at an elevated temperature, along with the finer samples, in the manner indicated above, its inferiority was at once manifest. The facts in this case were that the inferior charcoal readily yielded *all* its decolourative power at the low temperature, while the finer samples required the influence of heat to call their whole power into action.

Proximate Analysis of Coal.

An elementary analysis of coal teaches little with regard to the nature or practical value of the combustible. A proximate analysis, on the contrary, enables us to learn something in regard to the real nature of the coal. The moisture and ash are not only diluents of the fuel, but are in themselves obstacles to its effectiveness; the vapourisation of the moisture causes a serious loss of heat, whilst the ashes, by hindering complete combustion and by the heat they contain when dropped through the grate, constitute another loss. By furthermore determining the total amount of volatile matter we learn both the percentage of coke in the fuel and the amount of carbon (fixed combustible), and bitumen (volatile combustible matter). Although neither of these two products can be considered as simple chemical compounds, it is nevertheless of the utmost practical importance to know these two quantities, because of the great value of coke and gas in manufactures. The proximate analysis of coals has been worked out very fully by Professor G. Hinrichs. Before he instituted his researches no investigation as to its accuracy, nor the best method of conducting the work, was known. In Europe reliance seems to be placed almost exclusively on elementary analysis, whilst in the Government Surveys of the United States proximate analyses seem to have been almost as exclusively practised. But while the former may readily be turned into approximate determinations of the heating effects of the fuel, the latter have never been used for such purposes, nor, until Professor Hinrichs's researches, was it at all apparent that they ever could be thus made useful. It is evident that the useful applications of coal demand such an analysis, and it was therefore necessary for a rather extensive and thorough search into the method itself to be instituted, in order to study its exact value.

It is easily seen that the following elements will modify the result of the amount of volatile matter driven off from a sample of coal contained in a covered platinum crucible:—Weight of coal and of crucible; degree and duration of heat; condition of coal. But notwithstanding all these

elements, this determination admits of an accuracy of one-tenth of a per cent, equal to that of weighing a gramme exact to the milligramme.

The sample of coal used in these preliminary experiments was not selected, but taken at random. From this sample a very pure piece, free from any visible admixture of either gypsum or pyrites, was selected. Its specific gravity was found to be 1·328.

Determination of the Volatile Matter.—A common Bunsen burner is used for producing a red heat, and also a gas burner with six jets, surmounted by a French *soufflet cylindrique*, for obtaining a white heat, care being taken to keep the gas-cock in the same position by means of an arm of 10 inches in length. These two sources of heat are denoted respectively "B B," and "Blast."

The time is measured by means of a small sand-glass, running exactly three and a half minutes; this duration is denoted by *t*. Thus BB, *t*, means that the crucible was exposed to the constant flame of the Bunsen burner during three and a half minutes.

Influence of Quantity of Coal.—1. Coal pulverised, not dried; heat BB, *t*; cooled and weighed; then blast, *t*; then weighed again.*

N. of Exper.	Weight.	Volatile, per ct.	Deviation.	Crucible.
d	5·360	48·24	−1·14	19·2
n	1·910	49·58	+0·20	19·2
e	1·147	49·87	+0·49	11·6
o	1·031	49·85	+0·47	9·4
	Mean	49·38		

2. Coal in small fragments; heat as in 1.

h	3·743	48·30	−0·94	19·2
g	1·130	50·18	+0·94	9·4
	Mean	49·24		

For the same heat, the amount volatilised is the greater the smaller the mass heated; whether the coal is in small fragments or pulverised hardly makes any difference; but since the bitumen passes off more regularly when the coal is pulverised, while, when in fragments, slight explosions sometimes occur, the coal should be pulverised, for the determination of the bitumen.

3. Coal, pulverised, between 1 and 2 grms.; heat as above.

N. of Exper.	Weight.	Volatile, per ct.	Deviation.	Crucible.
n	1·910	49·58	−0·19	19·2
e	1·147	49·87	+0·10	11·6
o	1·031	49·85	+0·08	9·4
	Mean	49·77		

* Weight = coal taken in grammes; crucible = weight of the same. Deviation per cent from the mean given. These quantities are given in the same order in all subsequent tables, unless stated otherwise.

giving, as probable error of a single determination, only 0·108 per cent, or only 1 milligramme for 1 grm. of coal. This is not greater than that of the weighing itself, in which fractions of a milligramme were usually neglected.

4. Coal, pulverised (new portion), and between 1—2 grms.; heat, BB, *t*; immediately thereafter blast, *t*, without cooling.

N. of Exper.	Weight.	Volatile, per ct.	Deviation.	Crucible.
a'	1·160	50·86	+0·14	9·4
n'	1·040	50·58	−0·14	11·0
	Mean	50·72		

From 3 and 4 it is concluded that if the substance taken is from 1 to 2 grms., the result will be constant for the same mode of heating.

Influence of Drying the Coal before Ignition.—5. Coal fragments; heat, BB, *t*; not cooled; blast, *t*, with the probable error of one single determination, 0·45.

N. of Exper.	Weight.	Volatile, per ct.	Deviation.
t	1·361	48·49	+0·76
u	1·060	47·26	−0·47
v	1·030	47·43	−0·30
	Mean	47·73	

Comparing this with 4 (same heating), it appears that about 3 per cent less is volatilised by previous drying, and also that the accuracy of one determination is four times less than when the coal is ignited without previous drying. In the arts, the coal is not artificially dried before coking. For all these reasons, the amount of volatile matter is best determined on undried coal.

6. In general, it was found, as means—

4 dried coals gave 47·97 per cent volatile
10 undried „ 49·87 „ „

confirming the above.

Influence of Cooling after the Ignition over the Bunsen Burner, and before the Ignition over the Blast-Flame.—7. Coal, pulverised, not dried; heat, BB, *t*; then blast, *t*, without cooling.

N. of Exper.	Weight.	Volatile, per ct.	Deviation.
x	1·314	49·01	−0·02
y	1·156	49·05	+0·02
	Mean	49·03	

which, compared with the corresponding case, 3, giving the mean 49·77, and maximum deviation 0·19, shows that by the intermediate cooling about ¾ per cent more is volatilised. This probably is due to the fact that

the crucible upon cooling is filled with atmospheric air, which, upon renewed ignition, must burn a corresponding amount of coal.

Influence of Repeated Heating, the Crucible being after each Ignition Cooled and Weighed.—8. Coal $= r = 1·628$, in crucible 19·2, was dried, then ignited (BB, *t*), and lost 41·77 per cent. Being ignited again in the same way, it lost 2·76 per cent, or, in all, 44·53. Being successively ignited seven times, BB, each time for six minutes, the total loss was 52·39, or, on the average for each of these six minute BB ignitions, 1·12 (two of the determinations nearest this average were 1·06 per cent).

Hereafter the same was exposed to the blast five times for three and a half minutes; the volatile passed off amounted to 57·31, giving for each of these last ignitions the average loss of 0·98 per cent.

It now had been ignited fourteen times, each time having been cooled and weighed; and we have fourteen ignitions, 57·31 volatile—first ignition, 41·77 volatile; hence, average for each of the thirteen ignitions, 1·195, or 1·2 per cent.

This series of experiments shows that it is impossible to heat coal until no further loss is sustained; for it is apparent that each heating, after complete cooling, produces, on the average, more than the additional volatilisation of 1. On 1 grm. of coal taken, 1 per cent carbon burnt requires about 30 milligrammes, or 20 c.c. of oxygen. We may, therefore, consider these excesses almost equal losses due to a real combustion.

Influence of Protracted Heating.—9. Coal, pulverised, not dried; heat, always first BB, *t*; and then immediately, without cooling, transferred to blast-lamp.

No.	Weight.	Blast.	Volatile.	Difference.	Difference per minute.
$a'+n'$	(mean)	3 min.	50·72	0·57	0·19
c'		6 ,,	51·29	1·04	0·35
b'		9 ,,	52·33	1·95	0·65
d'		12 ,,	54·28	2·93	0·16
k'		30 ,,	57·21		

By comparing each with the first mean, we obtain for each minute blast after the first three, respectively—

0·24 0·39 0·27 0·20

showing less difference than the above.

The volatilisation, after the first three minutes' blast, is therefore increasing ¼ to ⅜ per cent for six minutes, and then very slowly decreasing to about ¼ per cent for half-an-hour. At this rate the loss is 12 per hour.

It is apparent that the loss is less than when cooled in the intervals, but it proves that a slight current of air must get at the coal in the covered crucible.

At any rate it is demonstrated, that the rule which is sometimes given, to heat until no further loss is sustained, demands an impossibility.

Influence of the Degree of Heat.—10. Coal, pulverised, not dried; heat, BB, *t*; cooled and weighed; then blast, *t*; cooled and weighed again.

After B B.

N. of Exper.	Weight.	Volatile, per ct.	Deviation.
n	1·910	48·08	+0·42
e	1·147	47·69	+0·03
o	1·031	47·23	−0·43
	Mean ..	47·66	
	Prob. error	0·284	

After Blast.

N. of Exper.	Volatile per ct.	Deviation.
n	49·58	−0·18
e	49·87	+0·11
o	49·85	+0·09
Mean ..	49·76	
Prob. error	0·108	

showing that the higher temperature gives the most accurate results.

Result.—From these experiments it is concluded—

The total volatile matter of coal is determined with accuracy (1 mgr. on 1 gr. coal), by taking 1 to 2 grms. of undried, pulverised coal, heating it for three and a half minutes over a Bunsen burner (bright red heat), and then immediately, without cooling, for the same length of time, over a blast gas-lamp (white heat).

Determination of the Moisture.—A flat-bottomed iron pan, of 20 centimetres in diameter, is filled evenly to the depth of 1¼ centimetres with sand, and the latter is covered with a copper plate, on which the watch-glass containing the coal is placed. A thermometer (scale to 370° C.) is, by means of an india-rubber stopper, inserted in an iron arm of the tripod supporting the iron pan, and held with its bulb about half a centimetre above the copper plate. By means of a Bunsen burner it is found very easy to keep the thermometer perfectly constant at 115° C. This apparatus is a good substitute for Fresenius's iron plate.

The coal to be dried is finely pulverised, direct experiments having shown that the application of fragments is not only very much slower, but also erroneous, on account of the peculiar property of bituminous coal treated of below.

These results show that the loss (called moisture) decreases regularly

after the first hour of drying, that is to say, while the coal loses in weight during the first hour, it steadily gains in weight thereafter. It appears, furthermore, that the accuracy of a determination, expressed in the smallness of the deviations from the mean, is greatest at the end of the first hour of drying, least after about three hours of drying, and thereafter increases again.

On account of these peculiar properties of bituminous coal, Professor Hinrichs advises that the loss in weight of the finely-pulverised coal after one hour's drying at a temperature between 105° and 110° C., should be put down as moisture.

On the Slow Oxidation of Coal.—This increase in weight after the first hour's drying was found in all Iowa coals. It was also found to occur in a sample of coal (Steinkohle) from Benthen, Silesia, which showed a loss of 3·62 per cent at the close of one hour, and in four further hours' drying gained again 0·42 per cent. It was not noticed in brown coal from Bilin, Bohemia, nor in anthracite from Pennsylvania. It is, therefore, probable that it is a property peculiar to pit-coal.

Pyrites might well be the cause of this phenomenon; the red ashes obtained in many cases may well be ascribed to pyrites disseminated through the coal in invisible particles.

From an examination of a large series of analyses, it has been found that the more ferruginous ash does correspond to a slightly greater increase in weight; but it is noticed also that this difference is but very small as compared to the total amount of increase, being only one-fifth to one-third of the whole. Arranging these coals in the order of this hourly increase, it is found that the colour of the ashes do not at all form a regular series from white to red, as it ought to be, if this increase mainly depended upon the oxidation of the pyrites.

The greater increase of the pyritic coals is accounted for by the oxidation of the pyrites they contain; the comparatively great increase of coals giving a pure white ash seems to force the conclusion upon us that the bitumen of the coal itself oxidises, and that to this oxidation the main increase of all these bituminous coals must be ascribed. Bearing in mind the deportment of bituminous coal from Silesia, anthracite from Pennsylvania, and brown coal from Bohemia, it seems not unlikely that this is another characteristic chemical difference between bituminous coals and other fossil coals.

Determination of the Ash.—The best way to determine the ash in coal is to coke the finely pulverised coal in a small platinum dish (weighing about 8 grms.), with subsequent incineration of this coke in the same vessel. The incineration takes place with great ease and rapidity, and the results are perfectly satisfactory.

Determination of Specific Gravity.—Coarse fragments, freed by means of a sieve from all small particles, and averaging 1-10th c.c. in volume, are introduced into a fifty-gramme flask provided with a thermometer stopper. The constants for this flask for temperatures varying from 50° to 80° F. are previously carefully determined.

The given sp. gr. corresponds to the coal perfectly soaked, so that all its pores are filled with water. That requires, on the average, 12 hours, permitting two determinations per day, one in the morning, another in the evening.

That this precaution is important may be seen from the following example:—2·760 grms. coal gave the sp. gr. 1·309 at 64° F., immediately after filling the flask with water; after about 12 hours soaking, the sp. gr. had increased to 1·328, for the same temperature. According to this latter determination, a cubic foot of this coal would weigh 82·76 lbs.; according to the former, only 81·58, or 1·18 lbs. less. This shows a considerable degree of porosity of the coal, and indicates the absurdity of giving the weight in pounds of a cubic foot of coal with four decimals, although no statement in regard to temperature or time of weighing is made.

Calculation of Results.—It may be sufficient here to state that, besides the percentage composition of the coal, it is proper to reduce the composition to the combustible = 100, in order to obtain a proper comparative estimate of the character of the fuel itself (in regard to the proportion of bitumen and carbon), and of the amount and quality of the impurities (ashes and moisture). It has also been shown that, for considerable areas of the coal-field, the sum of the constituents on the scale of combustible = 100 is the proper caloric equivalent, and that the percentage of the combustible in the fuel gives a proper estimate of its value.

Assay of Coal before the Blowpipe.

The blowpipe method is well adapted to the assaying of coal. Not only does the portableness of the apparatus make it very convenient for use away from home, wherever the balance can be set up; but its use at home is quite as satisfactory on the score of exactness as the assay with the muffle or retort, or large platinum crucible and large balance. Mr. B. S. Lyman gives the following directions for carrying out this assay:—

Besides the ordinary pieces of the blowpipe apparatus, as made at Freiberg, all that needs to be made expressly for the coal assay is a small covered platinum crucible of the same size and shape as the clay crucibles of that apparatus; and there must be a little ring for the crucible to stand on, of German silver, about three-eighths of an inch across and half that in height. Such a crucible cover and ring weigh about 2¼ grammes more than the ordinary metallic cup that rests on the pan of the balance;

the crucible and ring without the cover weigh less than 2 grammes more than the cup. If it be desired to determine the amount of hygroscopic moisture in the coal, a small drying bath must be made too; but the hygroscopic water in ordinarily well dried coals (not brown coals) is of little importance.

The size of the crucible allows the coking of 200 to 600 or more milligrammes of coal, according to the dryness of the coal and the extent of its swelling up when heated; and as the blowpipe balance weighs within 1-10th of a milligramme, it is easy to weigh within much less than 1-10th of one per cent of the amount of coal assayed, much nearer, in fact, than the exactness of the coke assay in other respects. In this point, indeed, the blowpipe assay is quite as good as the assay with the larger balance, especially the muffle assay, where the coal must be brushed into a clay receptacle after weighing, and the coke or ashes brushed off from it before weighing; while here the crucible is weighed each time without removal of its contents, and without danger, therefore, of losing anything or adding any dust. It may be objected that the smallness of the amount of coal that can be assayed with the blowpipe makes it a less trustworthy indicator of the general composition of the coal than a larger assay; but the size of the lumps or powder assayed may be made finer accordingly, so that when mixed up, an equally just sample of the whole mass would be got for the small assay as for the large.

Any one who has a little experience, both in the use of the blowpipe and in the ordinary muffle assay of coal, will scarcely need any further teaching for the coal assay with the blowpipe. For others, it is worth while to say that the coal may be assayed either in a fine powder or in little lumps, and either with a slowly increasing or with a quickly increasing heat. A quick heat will give less coke by several per cents, but will often make a dry coal cake together that would not cake with a slow heat. The cover of the crucible should be left open a little crack, for the easy escape of the gas, but covered enough to prevent any flying off of solid material. The heat should increase to redness, and as soon as the escaping gas stops burning the heat should be stopped. As some coals part with their gas more quickly than others, of course no definite time can be fixed for heating all coals; but the burning of the gas is a good enough sign. Care should be taken not to let the coke take up moisture from the air before weighing, as it will quickly do if it has a chance. Of course, owing to the different effect of quick or slow heat, a certain uniformity of result, even with perfectly uniform samples of coal, can only be got, without error, by practice and by mechanical skill, by reproducing with nicety the same conditions in successive assays.

After the coke has been weighed, it can be heated again with very free access

of air, say with the crucible tilted to one side, with the cover off, until everything is thoroughly burnt to ashes; and these should be re-heated until no change for the less is made in the weight. With free burning, soft (semi-bituminous) coals this burning to ashes is very slow, so that it is very fatiguing or even impossible to carry it out with the blowpipe; but in that case the crucible may be heated over a Bunsen gas burner or an alcohol lamp, and left to glow for hour after hour. The coking is far more conveniently done in the same way than by blowing with the mouth.

As an illustration of the degree of accuracy which this method may be expected to give, the author adduces a pair of blowpipe assays, made five years ago, of some West Virginia asphaltum, that seemed itself to be much more uniform in composition than coal from different benches in one bed is apt to be:—

	Volatile Matter.	Coke.	Ashes.
No. 1	47·29 per cent	52·71 per cent	1·65 per cent
No. 2	46·93 "	53·07 "	1·81 "
Mean	47·11 "	52·89 "	1·73 "

Estimation of Sulphur in Coal and Coke.

Mr. Crossley has drawn attention to the fact that the process of determining sulphur in coke, &c., by boiling in nitric acid gives results much below the truth. In the same sample he found the process of fusion with nitre, chloride of sodium, and carbonate of potassium gave 0·603 per cent, whilst boiling with nitric acid yielded only 0·477, whilst in another sample fusion gave 1·23 per cent, and boiling with nitric acid 0·93 per cent. He has arrived at the conclusion that the cause of this loss is not that some of the sulphur escapes oxidation, but that a portion is driven off by evaporation to dryness. Upon adding a little nitrate of potassium to the nitric acid, for the purpose of fixing the sulphuric acid formed, and thus prevent its volatilisation on evaporation to dryness, the results appear to be as accurate as those yielded by the fusion process.

Valuation of Coal for the Production of Illuminating Gas.

Take 100 grs. of the coal in small lumps, so that they may be readily introduced into a rather wide combustion-tube. This is drawn out at its open end (after the coal has been put in) so as to form a narrow tube, which is to be bent at right angles; this narrower open end is to be placed in a wider glass tube, fitted tight into a cork fastened into the neck of a somewhat wide-mouthed bottle serving as tar vessel (hydraulic main of the gas-works). The cork alluded to is perforated with another opening, wherein is fixed a glass tube, bent at right angles, for conveying the gas, first through

a chloride of calcium tube, next through Liebig's potash bulbs containing a solution of caustic potash, having oxide of lead dissolved in it. Next follows another tube, partly filled with dry caustic potash, and partly with chloride of calcium; from this last tube, a gas-delivery tube leads to a graduated glass jar standing over a pneumatic trough, and acting as gas-holder. Before the ignition of the tube containing the coal is proceeded with, all the portions of the apparatus are carefully weighed, and next joined by means of india-rubber tubing. After the combustion is finished, which should be carefully conducted, so as to prevent the bursting or blowing out of the tube, the different pieces of the apparatus are disconnected and weighed again. The combustion-tube has to be weighed with the coal after it has been drawn out at its open end, and with the coke after the end of the combustion when it is again cold; and for that reason care is required in managing it. We thus get the quantity of tar, ammoniacal water, carbonic acid, and sulphuretted hydrogen (as sulphide of lead); and the gas is measured by immersing the jar in water, causing it to be at the same level inside and out. Empty the Liebig's bulbs into a beaker, and separate the sulphide of lead by filtration, wash carefully, dry at 100° C., and weigh. From the sulphide of lead the sulphuretted hydrogen present is calculated. This process, devised by the late Dr. T. Richardson, of Newcastle-on-Tyne, was found by him to yield very reliable results, so as to be suitable for stating what quantity of gas a ton of coal thus analysed would yield.

Coal Gas.

Detection of Air in Coal Gas.—Ten parts by weight of anhydrous sulphate of protoxide of manganese are put into a two-necked Woulf's bottle, and twenty parts of warm water then added to dissolve it. To this mixture is immediately added a solution of ten parts by weight of Rochelle salt, dissolved in sixty parts of water; the thorough mixing of the fluids is promoted by well shaking of the bottle, after this a quantity of a solution of caustic potash is added, sufficient to render the fluid quite clear. Immediately after this perforated corks fitted with very tightly-fitting glass tubes, are placed in the necks of the bottle, which should be entirely filled with the mixed fluid just alluded to. One of the glass tubes—the inlet tube for the gas to be tested—should just dip a little under the upper level of the fluid; the outlet tube, on the other hand, should only reach half way the perforation of the cork. A very slow current of gas is now made to pass through the fluid, and kept going for at least a quarter of an hour and at most one full hour.

In case the gas is quite free from atmospheric air, the fluid in the bottle will remain quite clear; if traces even of air are present, a faint colouration

of the liquid will soon become apparent; with a larger proportion of air present in the gas, the fluid will soon be coloured, first light brown and afterwards intensely black. Since these changes of colour are due to the oxidation of the manganese, it is evident that every care must be taken to avoid the presence or access of accidental air; the fluid in the Woulf's bottle should reach the cork. It is best to cool the bottle during the experiment with ice, if at hand, otherwise with very cold water; the current of gas must be slow.

Estimation of Sulphuretted Hydrogen in Coal Gas.

An apparatus contrived by Dr. Wagner is used at the Munich Gasworks, to indicate the amount of sulphuretted hydrogen contained in crude gas. The following description is from the "Journal of Gas-lighting":*—

The apparatus consists of two glass flasks, E and A, a glass pipe, B, fixed upon a stand, and an aspirator. The first flask, E, contains a little acetic acid, for the absorption of the ammonia contained in the gas, and for the reception of the tar. The inlet pipe, *a*, is bent at an obtuse angle, to allow the condensed tar to flow into the flask, and after passing through an india-rubber stopper, the pipe descends to near the bottom of the flask, and dips into the acetic acid. The outlet-pipe, *b*, on the contrary, does not penetrate further than to within a short distance below the inner surface of the stopper, and is connected with the second flask, A, into which it enters, descending to nearly the bottom of it, by two bends and proper inclines. The second flask is about half filled with a solution of acetate of lead, made acid by acetic acid. The outlet-pipe, *c*, of this flask is at its upper end bent downwards, and is connected by an india-rubber tube with another smaller glass pipe, *d*, which passes through an india-rubber stopper, *e*, and penetrates into the pipe B to its lowest point, terminating in a fine end, so as to prevent the gas coming out otherwise than by a very narrow passage and in small bubbles. The pipe B is about one metre long, and, as shown in the woodcut, is also filled with a solution of acetate of lead. While the left extremity of this pipe is closed by the stopper, *e*, its right has a globe, *f*, at the end, for the deposit of any fluid that may have been carried over; and in continuation therewith is a glass tube, through which the gas takes its course to the aspirator, C. This aspirator, which in this instance has a capacity of twelve litres, is closed by means of an india-rubber stopper, through which passes the inlet-pipe, *g*, bent at the top, the extreme end of which, going downwards, is connected with the glass tube near the globe, *f*, by an india-rubber tube. At the bottom of the aspirator a small lateral pipe is inserted, with an india-rubber tube, the latter being provided with a pressure-cock, together with a thumb-screw, for the purpose of discharging the water.

* See also the "Chemical News," March 8, 1867, vol. xv., p. 112.

Fig. 8.

When the apparatus is used, the gas is admitted by a connecting pipe between the hydraulic main and the condenser—nearest, however, to the former.

The cast-iron pipe is drilled at the upper part, and the ¾-inch outlet lead pipe is carried upwards about 2 feet perpendicularly to convey back into the cast-iron pipe a portion of the tar carried onward by the warm gas, but which soon becomes condensed. The lead pipe is then bent downwards, and carried about 10 feet in length to the experimental table, where it terminates with a stop-cock. A short india-rubber tube is drawn over this cock so as to allow of its being connected afterwards with the apparatus. Before an experiment takes place gas is allowed to flow freely for at least half an hour through the supply pipe, in order that the inner surfaces of the same may become completely covered with tar, thus insuring that the lead of the pipe does not decompose the sulphuretted hydrogen of the gas.

After filling both the flasks and the pipe in the manner before described with the absorbing fluids, and completely filling the aspirator with water, and making tight all the connections of the apparatus, the water is allowed, by opening the pressure cock, *h*, to flow out of the aspirator until atmospheric air in the form of bubbles is sucked up by the apparatus, and until the level of the water corresponds exactly with one of the marked lines of the aspirator. The cock, *h*, is then again shut for a short time, and the loose end of the india-rubber tube fastened to the supply pipe is then drawn over the glass pipe, *a*. It is of course premised that the pressure of the gas in the supply pipe is $=0$, as is the case in establishments where exhausters are used. Upon the connection being restored between the apparatus and the supply pipe, the pressure cock is again slightly opened, and the gas allowed to pass gently—say about 20 litres per hour—until the water level in the aspirator has descended to the line marked 1. The flow of the gas is kept up as uniformly as possible by the regulating screw of the pressure cock. As at each experiment from 40 to 50 litres pass each time, it is necessary that the above experiment should be repeated several times. The pressure cock and the cock of the supply pipe being again shut, the stopper of the aspirator is loosened, the aspirator again filled with water, and the entire operation repeated in the manner above described.

Where no exhausters exist, and where there is a pressure of several inches in the gas supply pipe, no aspirators are required, but a gas-meter is used instead.

In the first flask, E, filled with acetic acid, is collected the greater portion of the tar; no absorption of sulphuretted hydrogen takes place here, as the crude gas enters it at a high temperature. In the second flask, A, and also very slightly in the pipe B, a black precipitate is formed, composed partly of sulphide of lead, partly of tar. The latter, however, is apt to carry

down with it a considerable quantity of the solution of lead employed. In order to bring the precipitate thus formed into a condition to be weighed, it is first filtered, then well washed, and dried at a temperature of about 100° C., and put into a small porcelain dish. Fuming nitric acid is then repeatedly poured over it, also at a temperature of about 100° C., and this is continued until the black mass has become quite white. When this has taken place, the residue of the nitric acid is driven off by evaporation at 100°. By the above operation the sulphide of lead is converted into sulphate of lead, the tar is destroyed, and the lead carried down by the tar is changed into nitrate of lead. Nitrate of lead, on the contrary, is readily soluble. For this reason the white mass is washed with water in a porcelain dish, and the soluble nitrate separated by filtration from the insoluble sulphate of lead. The latter, after being properly washed and dried, is heated in a crucible and weighed as sulphate of lead, from which the sulphuretted hydrogen is readily calculated.

Detection of Disulphide of Carbon in Coal Gas.—Dr. Herzog detects this body in the following manner:—A solution is prepared by saturating absolute alcohol with ammonia gas. Then a concentrated aqueous solution of acetate of lead is made, and, to insure saturation, a small portion of the solid salt is left in contact. Both these fluids must be preserved in well-stoppered bottles.

The gas to be tested may be conveniently delivered from a length of vulcanised india-rubber tubing, to the end of which is adapted a narrow glass tube, about five or six inches long. Five drops of the acetate of lead solution are then mixed in a test-tube, with about sixty or seventy drops of the alcoholic ammonia. No precipitate will be formed providing the latter solution has not been allowed to absorb any carbonic acid.

The glass tube delivering the supply of coal gas is now immersed in the mixed solution to a depth just sufficient to allow the gas to be forced out by the existing pressure, and to escape in small bubbles. In the event of disulphide of carbon being present, the liquid becomes gradually coloured, and soon afterwards a yellowish-red precipitate is formed, which, by longer action, assumes a brownish colour. If carbonic acid exists in the gas, then a white precipitate is thrown down, which imparts to the yellow-red a somewhat lighter colour.

As a confirmatory experiment, the gas may be first passed through the alcoholic ammonia alone, and the lead solution subsequently added, when an orange-coloured precipitate, appearing either immediately or very shortly afterwards, will be formed if disulphide of carbon is present. In order to meet the objection that sulphuretted hydrogen may perhaps have occasioned this reaction, let some of the gas be first passed through a small quantity of the simple lead solution. The smallest trace of sulphuretted hydrogen

causes the blackening of the liquid, whereas disulphide of carbon does not alter it in the slightest degree.

It should be mentioned that if the yellow-red precipitate be allowed to remain under the fluid, it gradually changes colour, and becomes white after the lapse of about twenty-four hours. If, however, the precipitate be filtered immediately, slightly washed, and dried, it becomes a dark brown.

With regard to the explanation of the chemical reactions which occur in this process, the observations made by MM. Zeise and Debus may be considered to prove that, by the action of disulphide of carbon on ammonia, according to the concentration and temperature of the fluids and the proportion borne by the ammonia to the sulphide, so will the relative amounts of the products of decomposition vary. In concentrated solutions, and when ammonia is in excess, sulphocarbonate of ammonium and sulphocyanide of ammonium are formed; in dilute fluids and when sulphide of carbon is in excess, xanthonate of ammonium. Therefore, by this experiment one or other product will preponderate according to circumstances, dependent upon the larger or smaller quantity of disulphide of carbon contained in the gas. In any case, compounds of lead are formed corresponding to the ammonia compounds, which possess at first an orange-red and afterwards a golden-yellow colour.

Notwithstanding the complicated nature of the chemical reactions involved in the testing of gas by this process, its adoption is to be recommended on account of the practical simplicity which has attended the working of a great number of comparative experiments.

Detection of Sulphur in Coal Gas.—By forcing, by an ordinary blowpipe, the flame of coal-gas for about a minute on to distilled water containing a little acid chloride of barium, sulphate of barium is formed, and the presence of sulphur in the gas thus proved.

Dr. Letheby's Process for the Estimation of the Total Amount of Sulphur in Coal Gas.—We have long employed a contrivance of Dr. Letheby, which is a most simple and effectual means for estimating sulphur in gas. The objects are to effect the combustion of the gas in a strongly ammoniacal atmosphere, by which means the sulphurous acid is fixed by the ammonia as soon as formed, and to condense the sulphite of ammonium. These objects are accomplished in the following way:—After passing the meter, the gas goes through a bottle filled with pebbles moistened with dilute sulphuric acid, for the purpose of estimating any ammonia the gas may contain. The inlet pipe to this bottle is allowed to pass only 1 inch through the cork; the outlet pipe passes to the bottom of the bottle. The gas is thus forced through the pebbles from the top, which prevents any accumulation of salt about the inlet pipe. In place of this bottle, a tube, about 6 inches long, an inch and a half in diameter, and

drawn out at each end, may be used. It is filled, of course, with pebbles, moistened with sulphuric acid like the bottle, and may be placed horizontally. The gas thus purified from ammonia is consumed at the rate of about half a foot per hour in a Leslie's burner, which is placed under a long funnel-shaped tube. This tube is connected to one end of a large glass cylinder similar to those used for electrical machines, the other end of which is furnished with a piece of glass tube, about four feet long, joined in such a manner that any products of combustion condensed in it will flow back into the large cylinder.

The means by which ammonia is supplied to the burner are the following:—A wide-mouthed bottle filled with the strongest liquid ammonia, is placed immediately beneath the burner, and a funnel, with a short tin tube attached to it, is placed over the bottle in an inverted position. This short tube passes through the centre of the burner, so that the end of it is about 2 inches above the top of the flame. The draught produced through the whole apparatus, when the burner is alight, is sufficient to evaporate the ammonia in the bottle, which is discharged through the tube into the centre of the receiving tube over the burner, and about 2 inches above the flame. Immediate combination then ensues between the ammonia and the sulphur products of the consumed gas, and the resulting sulphite of ammonium is condensed, along with the water formed, in the large cylinder. After pouring out the solution, and rinsing out the cylinder and tubes, the sulphite is converted into sulphate of ammonium, and the sulphuric acid determined as sulphate of barium in the usual way.

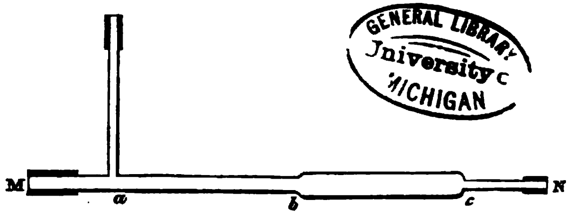
With this apparatus it is only necessary to observe two precautions—to burn the gas very slowly and to keep up the supply of ammonia. The latter is of the utmost importance.

Mr. Albert Ellissen speaks of this apparatus as follows:—In it the gas is consumed with a Leslie's burner, under the best practical conditions for a good oxidation of the sulphur contained in the gas. The consumption with that burner is so slow, that certainly during the ordinary burning of gas so perfect a combustion does not take place, and it may be made similar to the blue flame necessary in heating apparatus—a mode of consumption which should be taken into consideration in the use of gas for domestic purposes. The condensation of the sulphur products (sulphurous and sulphuric acids) in the glass cylinder is complete; experiments having proved that a sensibly greater amount of sulphur is not obtained by increasing the number of those vessels, nor by filling them with ammonia. The apparatus of Dr. Letheby has the additional advantage that the experiments may be made on the average quality of the gas manufactured during the day of twenty-four hours, and does not require the least superintendence. An interval of a few seconds is sufficient to empty the liquor collected in the

cylinder, the quantity of which affords a valuable check on the correctness of the progress of the experiment, and a fresh experiment may be immediately commenced by merely opening the stop-cock for the gas.

Mr. Valentin's Process for the Estimation of the Total Amount of Sulphur in Coal Gas.—Mr. Valentin has found that by passing a mixture of coal gas and air over spongy platinum, and then over a layer of soda-lime, both at a red heat, every trace of the sulphur is absorbed and arrested. He employs a platinum tube, MN, Fig. 9 (¼ size), 13 inches in length, which is heated on a small Hofmann's combustion furnace. The portion of the platinum tube marked *a b*, 5 inches in length and three-eighths of an inch in diameter, is charged with a cage constructed of a double roll of fine platinum gauze and filled with spongy platinum. The wider portion of the tube, *b c*, 4 inches in length and 5-8ths of an inch in diameter, contains the soda-lime. The air requisite to completely burn the gas enters through a narrow glass tube, connected by means of a small cork at M with the wide end of the platinum tube. A cap of an alloy of

FIG. 9.



silver and copper soldered to this part of the tube strengthens it sufficiently to prevent the thin platinum from being injured by a tightly fitting cork. The supply of gas to the tube passes through the narrow tube 4 inches long and 3-16ths of an inch in diameter, likewise capped, which is seen to branch off at a right angle from the portion of the main tube next to the anterior part of the platinum cage containing the spongy platinum. The products of combustion are allowed to escape at N, through the narrow platinum tube, *c* N. Connections for supplying gas and air are made by narrow, non-vulcanised, black india-rubber tubing.

The air is most conveniently supplied under slight pressure by means of a gas-holder, from which the air is expelled by displacement with water. Such gas-holders are found in most gas-works. A Low's motive-power meter may also be employed with great advantage, as it is capable of being regulated so as to give a supply of air sufficient for one experiment, whilst a small gas-holder would require to be re-filled with air once or twice during an experiment. The pressure from the gas-mains is at all times

sufficient to send the gas through the platinum tube. The respective proportions of gas and air are best regulated by means of meters, when the pressure-guage must of course show the same heights of water column; or the air may also be adjusted without having to pass through a meter merely by using a compression-cock on the narrow india-rubber tube.

Preparatory to an experiment the platinum tube is charged with pure soda-lime, by dropping in a lump sufficiently large to easily block up the narrow exit-tube. The whole of the wide portion of the tube, *b c*, is then gradually filled with loose pieces of soda-lime, of a size to enable the operator speedily to shake out the charge of soda-lime when the combustion is over. By gently tapping the platinum tube, held in an upright position whilst it is charged, the layer of soda-lime shakes down pretty completely, and is yet sufficiently porous to allow of a free and easy passage for the gaseous products of the combustion. The cage of spongy platinum is next introduced, and pushed down past the narrow branch tube. The gas and air connections are then made, and the platinum tube is placed upon a small combustion furnace, and heat applied to it from *a* to *c* by turning on the required number of gas burners at once. The platinum tube is best protected from the action of the gas flames by being kept imbedded in asbestos loosely spread in a thin layer along a trough made of tinned sheet iron. The supply of gas to the clay gas-burners should at no time be so great as to cause flames to shoot up above the burners or the tiles which cover the furnace. A dull red heat is sufficient, especially as much heat is generated inside the platinum tube by the combustion of the gas and air within the pores of the spongy platinum.

From 0·5 to 1 cubic foot of gas can conveniently be burned per hour, requiring from 5 to 10 cubic feet of air for its complete combustion. An experiment can thus be done in three to four hours, since as a rule 2 to 4 cubic feet of gas, burned in the manner described, yield sufficient sulphuric acid for an accurate weighing in the form of sulphate of barium.

The experiment over, the tube is allowed to cool in a slow current of air alone. The two ends are disconnected, and the cage of spongy platinum is drawn out by means of a copper wire having a little hook at one end. A stout bit of platinum wire in the form of a loop or ring may also be attached to the cage, for the more ready removal of the platinum cage. The latter is placed into a good-sized test-tube, and treated repeatedly with boiling distilled water, acidulated in the test-tube with a little dilute hydrochloric acid, in order to remove a little sulphuric acid which the spongy platinum retains. The soda-lime is next shaken out into a high beaker, and the tube washed out with hot dilute hydrochloric acid. This is most conveniently done by moving the platinum tube, held in a horizontal position, with its contents of dilute acid backwards and forwards in a small Bunsen gas

flame. The rinsings are poured over the solid soda-lime contained in the beaker. Loss from spirting must be guarded against by rapidly covering the beaker with a large watch-glass after each addition of hydrochloric acid, as long as an effervescence takes place. The soda-lime is completely dissolved by the application of a gentle heat, and the carbonic acid must be entirely driven off before the sulphuric acid can be precipitated by means of a solution of chloride of barium. On gently heating for some time, the precipitate falls down readily and completely, and may be filtered off after standing for a short time, and ignited and weighed as sulphate of barium.

The sulphuric acid can also be estimated volumetrically by means of a standard solution of chloride of barium.

The following are said by Mr. Valentin to be the advantages of this method of estimating sulphur in coal gas :—

1. *Perfect* combustion of the gas in a *close* vessel, at a very high temperature.

2. Complete and easy absorption of the sulphuric acid generated by the oxidation of the disulphide of carbon, in the *same* vessel in which it was generated.

3. No loss from imperfect condensation.

4. Possibility of completing an experiment in a few hours' time, or, as seems most desirable, during the time of the evening when the greatest consumption of gas occurs.

It is obvious that the process of combustion over spongy platinum is applicable to other gaseous mixtures containing sulphur compounds, such as the volatile products which escape during the process of incineration of various vegetable or animal matter, containing sulphur and phosphorus in combination with albumenoids, as well as in that of metallic sulphates and phosphates. There is, at present, no process known by which the *volatile* sulphur and phosphorus in albumenoid substances can be ascertained with anything like satisfaction, *independently* from the sulphur and phosphorus which are determined in the ash.

Carbonic Acid.

Estimation of Carbonic Acid in Natural Water.—M. Lory employs phosphate of copper dissolved in a very slight excess of hydrochloric acid. The phosphate of copper is obtained by precipitating a solution of chloride of copper with ordinary phosphate of sodium ; the precipitate is collected on a filter, well washed, and, after having been removed from the filter, it is suspended in water and dissolved by the addition of a few drops of hydrochloric acid. When this reagent is added to any water containing alkaline or earthy metals in the state of carbonates or bicarbonates, the result is, at first, the formation of a bluish coloured cloudiness, or turbidity ; by the

addition of a larger quantity of the reagent, this turbidity disappears and the liquid becomes clear again. This point having been reached, the quantity of the reagent employed will be proportional to the total equivalent of the bases present, and, consequently, to the carbonic acid which was combined with these bases.

In order to titrate the reagent, dissolve 0·265 grm. (equal to 1-200th of an equivalent) of perfectly pure and dry carbonate of sodium in water, and saturate this solution with carbonic acid, in order to convert it into bicarbonate; excess of carbonic acid does not at all affect the reagent. 4·4 c.c. of this solution in 1 decilitre of pure water should produce, by the addition of the copper liquor, the reaction already alluded to, and these 4·4 c.c. correspond to 0·220 grm. of carbonic acid.

This reagent is unchangeable and easily prepared, and is effectual no matter what quantity of chlorides, sulphates, &c., be contained in the water; it may even be employed for the alkalimetrical estimation of very dilute liquids; but it should be remarked that the reaction is much more exact with bicarbonates than when the bases exist as neutral carbonates or free alkalies. By combining this quick and simple test with the test by the standard solution of soap, both in the natural water and also in the same water after boiling, the most important elements for the appreciation of its ordinary and hygienic qualities will be obtained.

Estimation of Carbonic Acid in Artificial Mineral Waters.—In these waters the gas is present under considerable pressure. Mr. H. Napier Draper has devised the following apparatus by means of which the entire quantity of gas is easily and simply estimated.

1 is a tube of strong brass furnished at A with a screw, and tipped at B with a sharp steel ferule. This tube is open at both ends, and is pierced at C with two small holes.

2 is an accurately ground stop-cock, which can be screwed on to A, No. 1.

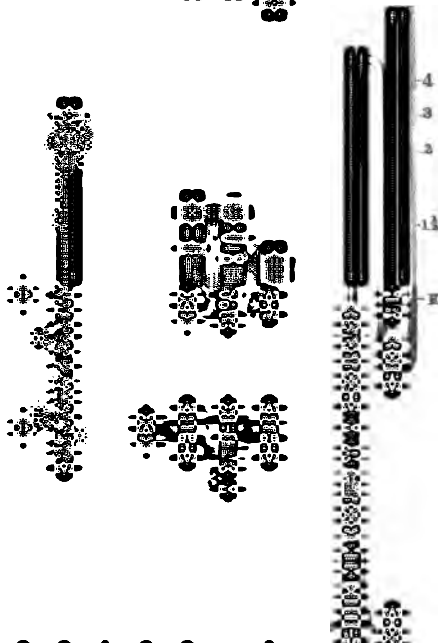
3 is a handle like that of a gimlet, screwing on to the other end of the stop-cock.

4 represents an air-pump syphon-gauge, of stout glass tube, securely cemented into a short brass tube, which is also provided with a screw, the thread of which coincides with those of the stop-cock and the tube No. 1. Mercury is poured into this tube and adjusted to the level E E'. The space E' F is then graduated, as shown in the figure, by first dividing it into two equal portions and marking the point of division 2. The lower space is then subdivided in the same manner, and the separating line marked 1½. The mark 4 is similarly obtained by dividing the upper space, and the 3 is placed at a point equidistant from 2 to 4.

There are two methods of using this apparatus. The first is more suitable in cases where great accuracy is required; the second is more practically

[illegible] seous contents of [illegible] consist wholly of [illegible]

[illegible] de of barium is [illegible] half its volume of [illegible] o become clear by [illegible] h in the following [illegible]



[illegible] uch more fluid as is [illegible] ith a cork through [illegible] e flask. About two [illegible] oured into the flask [illegible] -cock being adjusted [illegible] ee extremity of the [illegible] te the cork of the [illegible] ar below its under

surface. It is used, in fact, precisely as an ordinary cork borer. The handle is now removed and the stop-cock connected with the glass tube which passes into the flask, by means of a piece of vulcanised tubing about six inches long. The stop-cock is next turned on just so much as will allow the gas to bubble slowly through the solution of ammonia. The whole is left in this position for twelve hours, by which time all the gas not held in solution at the ordinary pressure will have been absorbed. That which is still retained by the fluid may either be expelled by heating the bottle placed in water, or the entire fluid may be mixed with the contents of the flask.

The carbonic acid can now, of course, be estimated by mixing the solution from the flask with about an ounce of the ammoniacal barium solution above-mentioned, gently heating, separating by filtration, and drying and igniting the precipitated carbonate of barium as usual. If the whole of the aërated water has been transferred to the flask, and if it contain carbonates or sulphates, or any earthy or metallic base, the weight of these must be deducted from that of the precipitate.

Approximate and Rapid Method of Estimation with this Apparatus.— This method of estimation cannot be considered as giving absolutely correct results; but from the facility with which it can be performed, it will be found useful where great accuracy is not required. It must be premised, however, that the necessary correction for temperature must be made; when this is done the results coincide very closely with those obtained by the first described method.

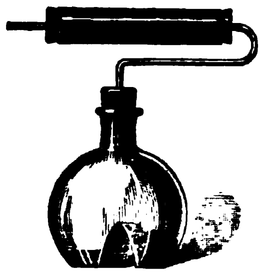
In this case the stop-cock, instead of being connected with the flask, is screwed into the mercury tube, 4, and gradually turned until fully open. Now as water dissolves at the ordinary pressure of 30 inches, its own volume of carbonic acid, and as the quantity dissolved at other pressures is directly proportional to the pressure exerted, it is clear that if we know the amount of this pressure and the volume of the water in which the gas is dissolved, we can, knowing also the weight of an equal volume of carbonic acid, determine by weight the quantity of the latter held in solution. Or, without knowing this latter number, we can express, as is most usual, the quantity of gas in cubic inches. Now it is also clear that as the volume of a gas is inversely as the pressure to which it is subjected, the mercury tube graduated as in the figure will show at a glance the number of atmospheres under which the carbonic acid is held dissolved.

Estimation of Carbonic Acid in Solid Carbonates.—Dr. Cameron employs an apparatus shown in Fig. 11. It consists of a light bottle, of the capacity of 75 centimetres. The lower part is divided into two compartments; in one of which the carbonate is placed, in the other the acid. By inclining the bottle, the acid may be allowed to flow over on the

carbonate as gradually as the operator pleases. One or two chloride of calcium tubes are inserted through the cork.

The use of anhydrous sulphate of copper, jointly with fused chloride of calcium, is preferable as a drier in case hydrochloric acid is used in the analysis.

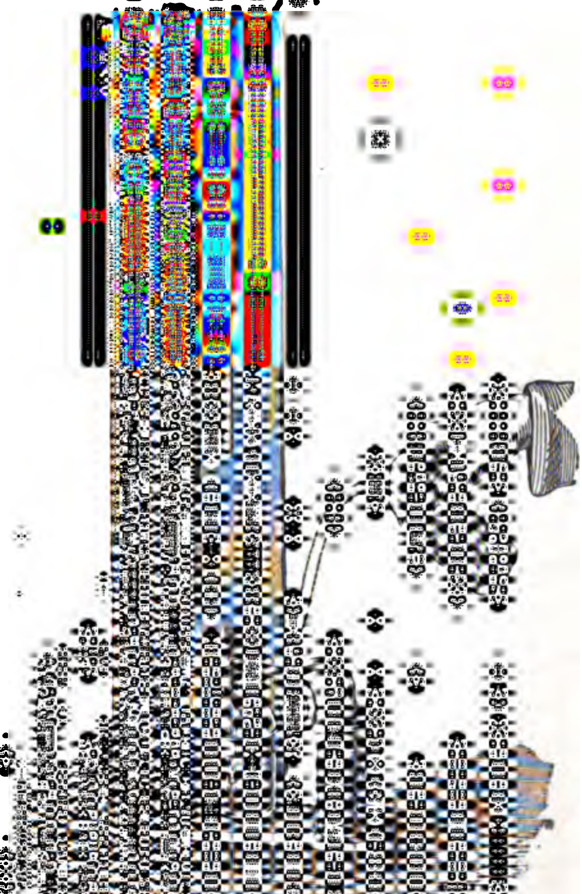
FIG. 11.



Volumetric Estimation of Carbonic Acid in Solid Carbonates, Animal Charcoal, &c.—Dr. Schiebler has devised a very perfect instrument which is adapted for the estimation of the quantity of carbonic acid contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the quantity of carbonic acid contained in animal charcoal. The principle upon which the apparatus is founded is simply this:—That the quantity of carbonic acid contained in carbonate of calcium can, according to well-known stochiometrical rules, be used as a measure of the quantity of that salt itself; and instead of determining, as has been usually the case, the quantity of carbonic acid by weight, this apparatus admits of its estimation by volume. It is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need scarcely possess any knowledge of chemistry. The analytical results obtained by means of this apparatus are very correct, provided care be taken to use the needful precautions.

The apparatus is shown in the annexed woodcut, and consists of the following parts:—(1). The glass vessel, A, serving for the decomposition of the material to be tested for carbonic acid, which, for that purpose, is treated with dilute hydrochloric acid; this acid is contained, previous to the beginning of the experiment, in the gutta-percha vessel, *s*. The glass stopper of A is perforated, and through it firmly passes a glass tube, to which is fastened the india-rubber tube, *r*, by means of which communication is opened with a three-necked tubulated bottle, B. The central neck

[illegible] communica-
[illegible] rubber tube
[illegible] a very thin



[illegible] very light and
[illegible] neck, q, of the

vessel B is shut off during the experiment by means of a piece of india-rubber tubing, kept firmly closed with a spring clamp; the only use of this neck of the bottle, B, arranged as described, is to give access of atmospheric air to the interior of the bottle, if required. The other opening is in communication with the measuring apparatus, C, a very accurate cylindrical glass tube, of 150 c.c. capacity, divided into 0·5 c.c.; the lower portion of this tube C is in communication with the tube D, serving the purpose of controlling the pressure of the gas; the lower part of this tube D ends in a glass tube of smaller diameter, to which is fastened the india-rubber tube, *p*, leading to E, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can readily be done by blowing with the mouth into V, and opening the clamp at *p*.

The following apparatus and reagents are also necessary:—A small and very accurate weight for weighing off the substances to be tested; a thermometer; hydrochloric acid; a solution of carbonate of ammonium; several small porcelain basins.

The main portion of the apparatus above described, with the exception, however, of the vessel, A, is properly fixed by means of brass fittings to a wooden board, as represented in the woodcut. The filling of the apparatus with water is very readily effected by pouring it through a suitable funnel placed in the open end of the tube D, care being taken to remove, or at least to unfasten, the spring clamp at *p*; in this manner the water runs into E, which should be almost entirely filled. Distilled water should be used for this purpose, as the filling only requires to be done once, the water always remaining in E as long as the apparatus is intended to be kept ready for use. When it is required to fill the tubes C and D with water, so as to reach the zero of the scale of the instrument, remove the glass stopper from A; the spring clamp at *p* is next unfastened, the air is then blown by means of the mouth into the tube V, which communicates with E; by this operation the water rises up into the tubes C and D, which thus become filled with that liquid to the same height. Care should be taken not to force the water above the zero of the scale at C, and especial care should be taken against forcing so much of the fluid up that it would run over into the tube *u*, and thence find its way to B, as in this case a total disconnection of all the parts of the apparatus would become necessary. If by any accident the water should have been forced up above the zero at C, before the operator had closed the spring clamp at *p*, this is easily remedied by gently opening that clamp, whereby the water is allowed to run off to E in such quantity as may be required to adjust the level of the fluid in C precisely with the zero

of the scale. The filling of the tube C with water has the effect of forcing the air previously contained in that tube into B, where it causes the compression of the very thin india-rubber ball placed within B; if it should happen that this india-rubber ball has not become sufficiently compressed and flattened, it is necessary to unfasten the spring clamp at *q*, and to cautiously blow air into B, through the tube, *q*, by which operation the complete exhaustion of the india-rubber bladder placed within B is readily performed. This operation is also required only once, because during the subsequent experiments the india-rubber bladder, K, is emptied spontaneously. It may happen, however, that while the filling of the tubes D and C with water is being proceeded with, the india-rubber bladder, K, has become fully exhausted of air before the water in C reaches the zero of the scale; in that case the level of the water in the tubes D and C will not be the same, but will be higher in D; it is evident, however, that this slight defect can be at once remedied by momentarily unfastening the spring clamp at *q*.

The apparatus should be placed so as to be out of reach of direct sunlight, and should also be protected against artificial heat, and sudden changes of temperature; the instrument is best placed near a north window, so as to afford sufficient light for reading off the height of the water in the tubes.

Hydrochloric Acid.—The acid required for the decomposition of the animal charcoal is poured into the vessel *s* for use during experiments. This acid need not be pure; the crude acid of commerce answers the purpose, provided it be diluted to a specific gravity of 1·120 at 17° C. For practical purposes it is sufficient to mix two parts by bulk of water with one part by bulk of commercial hydrochloric acid.

Carbonate of Ammonium.—In order to prepare the solution of this salt of the necessary strength, one part by weight of the ordinary carbonate of ammonium of the shops is dissolved in four parts of water, and to this one part of liquid ammonia is added. The salt is first coarsely pulverised and immediately after placed in a bottle provided with a well fitting glass stopper; the mixture of water and ammonia is next poured over the salt and the solution of the salt promoted by frequent shaking of the bottle. This solution of carbonate of ammonium is used for the purpose of converting into carbonate of calcium any caustic lime which might be present in the materials to be submitted to analysis.

Mode of Operating.—It is of the greatest importance that a good average sample, really representing the entire bulk of animal charcoal, be taken for investigation; this can be readily obtained by taking small samples, say a few ounces, from the filter (in sugar works) or from a cask, at various depths of the vessels containing the material; or, better still, if there be room, the charcoal should be placed in a heap on a large sheet of stout

canvas, and well mixed together, and samples taken from various parts of the heap. These, if wet (as will be the case with charcoal just removed from the filters), should be dried by suitable means, and afterwards the whole sample should be coarsely ground and thoroughly mixed, and a portion taken for the purpose of being ground up to a very finely divided powder, to serve the purpose of weighing a sample from. It is essential that the charcoal should be ground to a very fine powder, because this greatly promotes the decomposition by the acid.

There is supplied with the apparatus a metallic weight to serve as normal weight. This weight is placed in one of the pans of the balance (any balance, provided it be sensitive to from 1-8th to 1-10th of a grain, will answer the purpose); in the same pan a small porcelain basin is placed, and equilibrium is restored by means of small lead shot. As soon as the equilibrium is restored, the normal, or standard, weight is removed from the pan of the balance, and there is placed in the small porcelain capsule remaining in the pan as much of the sample of bone-black to be tested as is required to restore the equilibrium. When several experiments have to be made consecutively, it is better to arrange beforehand the joint tare weight of the normal weight, and of a watch-glass of suitable size, and to weigh off upon the latter the several samples. Dr. Schiebler recommends the transference of these weighed quantities to a porcelain capsule, because, according to his plan, the samples, *after* having been weighed, have to be thoroughly moistened with the solution of carbonate of ammonium already referred to, in order to convert any caustic lime which might happen to be present in the material into carbonate of calcium, but it is a decided improvement to moisten gently with the solution of carbonate of ammonium a sufficient quantity of the sample to be tested previous to weighing, to dry it, and to employ at last, for a few moments, a stronger heat short of redness (an air or fusible metal bath, heated to 240° C.), so as to obviate the chance of either an excess of carbonate of ammonium or of water being present, while, at the same time, the decomposition of the carbonate of calcium is guarded against. After the samples are quite cold, they are to be transferred to the flask or bottle A. Recent researches have shown that animal charcoal which has been once used for filtering purposes in sugar works no longer contains caustic lime, and the treatment with carbonate of ammonium can therefore be dispensed with in that case, and need only be employed with samples freshly made.

The experiment for the estimation of the carbonic acid is carried out in the following manner:—First the water in the tube C is made to stand exactly at the zero (0) of the scale; next the weighed sample of the bone-black to be tested is transferred, with great care and without loss, to the bottom of the bottle A, which should be perfectly dry inside and quite clean.

This having been done, the gutta-percha vessel, *s*, which should also be previously well cleaned, is filled with the hydrochloric acid above referred to, to within from $\frac{1}{2}$ to $\frac{3}{4}$ inch from the top, care being taken not to drop any hydrochloric acid on the outside of the vessel; the gutta-percha vessel is next placed within the bottle A in a slanting direction, as shown in the woodcut; after this the glass stopper is replaced at A, care being taken to slightly grease it and the inside of the neck of A, so as to secure a better air-tight fitting. The closing of A will (if all parts of the apparatus are properly tight) have the effect of slightly lowering the level of the water in C, below the zero of the scale, while the water will rise just as much higher in D; by loosening, for a moment, the spring clamp at *q*, the normal height is properly restored. The operator should very carefully guard against handling or touching A after it has been once closed, because, by so doing, the warmth of his hand will cause the expansion of the air in A, and thereby affect the proper action of the apparatus. In order to cause the hydrochloric acid contained in the gutta-percha vessel placed inside A to run on to the animal charcoal, placed on the bottom of A, as described, the flask, or bottle, A, is held by the neck, as shown in the woodcut. As soon as the acid comes into contact with the animal charcoal, the evolution of carbonic acid begins, and simultaneously the expansion of the very thin india-rubber bladder, K, while the water in the tube C sinks, and correspondingly rises in D. While the bottle A is held in the right hand, as already indicated, and gently moved about, so as to promote, as much as possible, the contact between the acid and the charcoal, the left hand is employed to gently open the spring clamp, *p*, in such a manner as to run off towards E just as much water as is required to keep the level in the tubes C and D at the same height; both these manipulations should be continued as long as any sinking of the level of the water in C is perceptible: in other words, as long as any carbonic acid is given off. After this has quite ceased, and no change is perceptible, or any motion of the water in the tubes just alluded to has taken place, the operation may be considered at an end, care being taken, however, to keep the levels in the tubes C and D at precisely the same height. This having been done, the next step is to read off the height of the water at the scale on C, and simultaneously the thermometer.

Correction of the Volume Read Off.—The Table (page 397) contains, in the first column, the figures 1 to 25, which correspond with the numbers on the scale fixed to C; the next nineteen vertical columns contain the figures indicating the percentage of carbonate of calcium sought at temperatures from 12° to 30° C. If, for instance, the experiment has been made at a temperature of 16°, and the reading of the scale at C corresponded to 9°, this indicates a quantity of carbonate of calcium of 9·03 per cent. Since,

however, every degree at c is divided into ten parts, it is quite possible to read off tenths of a degree, and the corresponding quantity of carbonate of calcium is also found by the aid of the table referred to, under the first nine figures of the column, by simply altering from the right to the left hand the decimal point; for instance, we have found at 14° C. 7·8° at the scale c; we therefore have for 7 units 7·09 per cent, and for 8-10ths 0·81 (because 8=8·11), making together, for 7·8, 7·90 per cent carbonate of calcium.

Illustrative Examples.—

9·4° read off at c, at a temperature of 19°=9·289 per cent of carbonate of calcium.

14·9° read off at c, at a temperature of 13°=15·056 per cent of carbonate of calcium.

12·3° read off at c, at a temperature of 24°=11·799 per cent of carbonate of calcium.

11·7° read off at c, at a temperature of 16°=11·702 per cent of carbonate of calcium.

It is, however, for all practical purposes, quite sufficient to make round numbers of the figures following the decimal point, and instead of 9·289 to read 9·30; for 15·056 to read 15·06; for 11·799 to read 11·8; and for 11·702 to read simply 11·7.

The calcimeter is invaluable in cases where the frequent estimation of carbonic acid is required. With a little practice, twelve or fourteen estimations may easily be made in an hour; and these, if upon the same finely-powdered sample, will, with ordinary care, be found to agree almost absolutely. The saving of time by this process over the most expeditious of the ordinary gravimetric methods will be found to be very great. Starting, in each case, with the sample in powder, the difference in time is such as easily to repay the first cost of the instrument by a few hours' work. As the instrument is supplied with a normal weight and tables of calculated results, no time is lost in after calculations. The volume of carbonic acid, and the temperature indicated by the instrument, are referred to the tables, where the percentage quantity of carbonic acid or carbonate of calcium is at once found. One great advantage of such an expeditious method as this is that there is no temptation to be satisfied with first results, as a few minutes suffice to repeat the process.

BORON.

Detection of Boron in Minerals.

After estimating the water of crystallisation, Professor Wöhler dissolves the mineral (tinkalcite) in hydrochloric acid, and after neutralising with ammonia, precipitates the calcium with oxalate of ammonium; concentrates

TABLE

For the Percentage Estimation of the Carbonate of Calcium Contained in Animal Charcoal, Calculated from the Volume of the Carbonic Acid.

Observed volume of carbonic acid.	Degrees of Temperature (Centigrade).																		
	12°.	13°.	14°.	15°.	16°.	17°.	18°.	19°.	20°.	21°.	22°.	23°.	24°.	25°.	26°.	27°.	28°.	29°.	30°.
1	0·80	0·80	0·79	0·79	0·79	0·78	0·78	0·77	0·77	0·77	0·76	0·76	0·76	0·75	0·75	0·74	0·74	0·73	0·73
2	1·88	1·87	1·86	1·86	1·85	1·84	1·83	1·82	1·81	1·80	1·79	1·79	1·78	1·77	1·76	1·75	1·74	1·73	1·72
3	2·95	2·94	2·92	2·91	2·90	2·89	2·87	2·86	2·85	2·83	2·82	2·80	2·79	2·77	2·76	2·74	2·73	2·72	2·71
4	4·01	4·00	3·98	3·96	3·94	3·93	3·91	3·89	3·87	3·85	3·83	3·81	3·79	3·77	3·75	3·73	3·71	3·70	3·68
5	5·07	5·05	5·03	5·00	4·98	4·96	4·93	4·91	4·89	4·86	4·84	4·81	4·79	4·76	4·74	4·71	4·69	4·67	4·65
6	6·11	6·09	6·06	6·03	6·01	5·98	5·95	5·92	5·89	5·86	5·83	5·81	5·78	5·75	5·71	5·68	5·65	5·63	5·61
7	7·14	7·12	7·09	7·06	7·02	6·99	6·96	6·92	6·89	6·86	6·82	6·79	6·75	6·72	6·68	6·65	6·61	6·58	6·56
8	8·17	8·14	8·11	8·07	8·03	8·00	7·96	7·92	7·88	7·84	7·80	7·76	7·72	7·68	7·64	7·60	7·56	7·53	7·49
9	9·19	9·16	9·12	9·07	9·03	8·99	8·95	8·90	8·86	8·82	8·77	8·73	8·68	8·64	8·59	8·55	8·50	8·46	8·42
10	10·20	10·16	10·12	10·07	10·02	9·98	9·93	9·88	9·83	9·79	9·73	9·68	9·63	9·58	9·53	9·48	9·43	9·39	9·34
11	11·20	11·15	11·10	11·05	11·00	10·95	10·89	10·84	10·79	10·74	10·68	10·63	10·57	10·52	10·46	10·41	10·35	10·30	10·25
12	12·20	12·15	12·09	12·03	11·98	11·92	11·87	11·81	11·75	11·69	11·64	11·58	11·52	11·46	11·40	11·33	11·27	11·22	11·16
13	13·20	13·14	13·08	13·02	12·96	12·90	12·84	12·78	12·72	12·65	12·59	12·53	12·46	12·40	12·33	12·26	12·20	12·14	12·07
14	14·20	14·14	14·07	14·01	13·94	13·88	13·81	13·75	13·68	13·61	13·54	13·48	13·41	13·34	13·26	13·19	13·12	13·05	12·99
15	15·20	15·13	15·06	14·99	14·92	14·85	14·78	14·71	14·64	14·57	14·50	14·42	14·35	14·27	14·20	14·12	14·04	13·97	13·90
16	16·20	16·13	16·05	15·98	15·91	15·83	15·76	15·68	15·61	15·53	15·45	15·37	15·29	15·21	15·13	15·05	14·97	14·89	14·81
17	17·20	17·12	17·04	16·97	16·89	16·81	16·73	16·66	16·57	16·49	16·41	16·32	16·24	16·15	16·07	15·98	15·89	15·81	15·72
18	18·20	18·12	18·03	17·95	17·87	17·79	17·70	17·62	17·53	17·45	17·36	17·27	17·18	17·09	17·00	16·91	16·82	16·73	16·63
19	19·20	19·11	19·03	18·94	18·85	18·76	18·67	18·59	18·50	18·40	18·31	18·22	18·13	18·03	17·94	17·84	17·74	17·64	17·55
20	20·20	20·11	20·02	19·93	19·83	19·74	19·65	19·55	19·46	19·36	19·27	19·17	19·07	18·97	18·87	18·77	18·66	18·56	18·46
21	21·20	21·10	21·01	20·91	20·81	20·72	20·62	20·52	20·42	20·32	20·22	20·12	20·01	19·91	19·80	19·70	19·59	19·48	19·37
22	22·20	22·10	22·00	21·90	21·80	21·70	21·59	21·49	21·39	21·28	21·17	21·07	20·96	20·85	20·74	20·63	20·51	20·40	20·28
23	23·20	23·09	22·99	22·88	22·78	22·67	22·56	22·46	22·35	22·24	22·13	22·02	21·90	21·79	21·67	21·55	21·44	21·31	21·20
24	24·20	24·09	23·98	23·87	23·76	23·65	23·54	23·43	23·31	23·20	23·08	22·97	22·85	22·73	22·61	22·48	22·36	22·23	22·11
25	25·20	25·08	24·97	24·86	24·74	24·63	24·51	24·39	24·28	24·16	24·04	23·91	23·79	23·67	23·54	23·41	23·28	23·15	23·02

the filtrate and estimates the boracic acid in the state of double fluoride of boron and potassium.

In the case of minerals like tourmaline, which contain fluorine and boron, the question is not so simple. The volatile matters may be determined by a process analogous to that employed in the case of fluoride of silicium; the fluoride of boron being changed into a mixture of fluoride of calcium and boracic acid. Unfortunately we do not know a method of estimating boron in mineral substances, especially if associated with fluorine and silicium; so that if we have fluoride of boron, fluoride of silicium, and alkaline fluorides, we can estimate the alkalies, but not the boron, silicium, and fluorine. In the absence of a quantitative method for estimating boron, we have an excessively delicate qualitative test. The best method of recognising the presence of boron, if no fluorine is present, is to mix the substance with a small quantity of fluoride of calcium and bisulphate of potassium, having previously ascertained that the two reagents do not contain boron; two experiments must therefore be made, one on the reagents, and the other on the substance mixed with the reagents. The mixture is slightly moistened, and held on the extremity of a perfectly clean platinum wire. Direct the reducing flame of the blowpipe on to the paste; at the moment when the mixture appears to boil the flame assumes a vivid green colour, characteristic of boron. When but little boron is present, this must not be tried in full daylight, and it should be viewed against a dead black background; the colour of the flame will then be easily detected.

Estimation of Boracic Acid.

In order to estimate directly the boracic acid contained in datolite, a borosilicate of calcium, Professor Wöhler proceeds as follows:—Place the mineral in a small tubulated retort, decompose it with hydrochloric acid, and distil the mixture to dryness; pour on to the residue the distillate (which contains boracic acid), and allow it to digest to separate the silica. In the liquid precipitate the calcium by means of oxalate of potassium, taking care not to add it in too great excess. Then after filtration and concentration, precipitate the boracic acid in the form of double fluoride of boron and potassium. For this purpose add a little potash to the material in a platinum capsule, then pour over the mixture a slight excess of hydrofluoric acid, and evaporate the solution to dryness. To remove the other salts it suffices to treat the mass with a moderately concentrated solution of acetate of potassium; then allow it to digest and throw on to a filter the double fluoride of boron and potassium, and wash it with the same solution of acetate. Then wash with dilute alcohol to remove the acetate of potassium. The double fluoride is dried at 100 C., and weighed.

Analysis of Borates and Fluoborates.

In solutions which contain only boracic acid and alkalies, Marignac determines the former as follows:—The solution is neutralised with hydrochloric acid, and chloride of magnesium, or preferably the double chloride of magnesium and ammonium, is added in such quantity that to one part of boracic acid at least two parts of magnesia are present. The liquid is now made ammoniacal, and finally is evaporated to dryness in a weighed platinum vessel. Should the addition of ammonia cause a precipitate which does not readily disappear in warming, sal-ammoniac must be added until the liquid becomes clear. During the evaporation it is well to add a few drops of ammonia from time to time. When the mass is dry it is heated to redness, then treated with boiling water; the residue is collected on a filter, and washed with hot water until the washings are not in the slightest degree affected by nitrate of silver.

This first residue contains, together with excess of magnesia, the larger part of the boracic acid. A small amount of the latter always goes into solution. The filtrate and washings are treated with ammonia and again evaporated, ignited, and washed as before. The second filtrate and washings are once more treated in the same manner, when great accuracy is required.

The three residues are ignited together in an open crucible as strongly as possible, and sufficiently long to decompose the traces of chloride of magnesium which they may contain. When they are weighed, it only remains to estimate the magnesia in them to learn by difference the quantity of boracic acid. This can be done either by dissolving in an acid and precipitating ammonio-phosphate of magnesium, or more rapidly by dissolving in a known volume of standard sulphuric acid at a boiling heat and determining the excess of acid by means of a standard alkaline solution.

Should an insoluble, heavy, grey residue remain on treating with acid, it must be collected and its weight deducted from that of the borate of magnesium; it will be platinum.

From insoluble compounds the boracic acid is obtained in solution by fusing with three times their weight of carbonate of sodium, and exhausting the mass with water. In case of silicates, the alkaline solution is digested with chloride of ammonium to precipitate silica.

When operating with a fluo-borate, the solution of the carbonate of sodium fusion is digested with sal-ammoniac to decompose a good proportion, but not all of the carbonate of sodium, and is then precipitated with a neutral or ammoniacal solution of chloride of calcium. The precipitate of fluoride and carbonate of calcium is washed—a matter easily accomplished—dried, gently ignited, treated with acetic acid, evaporated to dryness, and the pure fluoride of calcium collected, washed, and weighed.

The filtrate, after removing calcium by addition of carbonate and a few drops of oxalate of ammonium, may be treated as before described for the estimation of boracic acid.

SILICON.*

Decomposition of Silicates in the Wet Way.

A. **By means of a Fluoride and Acid.**—Mr. C. E. Avery finds that silica and silicates, such as felspar and glass, may be completely dissolved in the cold by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

When mixed with the fluorides of sodium, barium, aluminum, lead, or the double fluorides of these metals, the silicates in question can be readily decomposed by nitric, hydrochloric, or sulphuric acid, either concentrated or diluted with four volumes of water.

If strong sulphuric acid is used, a part of the silicon passes off as gas; if the dilute acid is used, portions of many silicates remain undissolved as insoluble sulphates.

The same decomposition of the silicates is effected, though less easily, by the action of oxalic, acetic, tartaric, and like acids, on the mixed fluoride and silicate. Carbonic acid, even as dilute as it is in the air, does the same thing but less rapidly.

Strong nitric acid gives a perfect solution and acts rapidly, dissolving a moderately fine powder of felspar or quartz in a few hours, even in the cold. The loss of silica is very slight if the experiment is properly conducted; hence, all the constituents of a siliceous mineral can be estimated in the solution produced.

In analysing the silicates in this way, it is best to use the fluoride of some metal which is not to be estimated in the analysis; since, if we use a fluoride whose metal is present in the mineral, we must know the weight of fluoride taken. Of the various fluorides those of barium and lead seem to be the most promising.

An objection to the use of fluoride of ammonium is that, as usually made, it contains sulphate of ammonium, so that insoluble sulphates might be formed and solution retarded.

If fluoride of sodium, as made from cryolite, were not so hard to purify, it would be well fitted for the analysis of silicates free from sodium.

B. **By means of Hydrofluoric Acid.**—Professor N. S. Maskelyne employs hydrofluoric acid for the analysis of refractory silicates. The process is conducted in an apparatus of the following construction:—A platinum retort, 30 c.c. in capacity, is fitted with a tubulated stopper of the same material, which reaches nearly to the bottom; a small tube entering

* For the detection and estimation of silicon in iron and steel see chap. v., p. 93.

the vertical tube of the stopper at an angle above the neck of the retort, conveys hydrogen to its interior. The vertical tube can be closed, either by a stopper of platinum or by a funnel of that metal, stopped in like manner at the top, and having a fine orifice at its lower extremity.

To the side of the retort, just below its neck, a straight delivery-tube is fixed, which in its turn fits into another platinum tube that, after taking a curve into a vertical position, is enlarged into a cylinder, which passes a considerable distance down a test-tube. The latter, into which the delivery-tube is fitted with a cork, holds 7·5 c.c., or 6·6 grms. of strong ammonia of the sp. gr. 0·88.

The gas-delivery tube inserted in the side of this receiver dips into some more ammonia in a second test-tube.

The pounded mineral, from 0·2 to 0·5 grm. in quantity, and a small platinum ball, are placed in the retort, and the stopper luted to it with gutta-percha, and cemented air-tight in its place with caoutchouc and gutta-percha varnish. The funnel, filled with perfectly pure hydrofluoric acid, is now introduced into the tubulure of the stopper, the tap opened, and the acid allowed to run down into the retort. This acid contains about 32 per cent of absolute hydrofluoric acid—that is to say, a funnel full of this reagent contains 1·12 grms. of acid, capable of rendering gaseous 0·84 grm. of silica, and of neutralising 0·95 grm. of ammonia. The funnel is now replaced by a little platinum stopper, and the orifice secured air-tight with gutta-percha varnish. Pure hydrogen is then allowed slowly to traverse the entire apparatus; the retort is placed in a water-bath at 100° C. for two hours, and occasionally slightly shaken to set the ball rotating. During the operation, a trace only of fluoride of silicon passes over.

The retort is next transferred to a paraffin bath, and the temperature is cautiously raised. At first hydrofluoric acid passes over, and at this point of the process the flow of hydrogen requires some attention to prevent regurgitation of ammonia. At about 130° C. the silica first becomes visible in fine flocks in the ammonia of the receiver, and in another minute the whole is cloudy.

In eight minutes, the rise of the thermometer to 145° C. has brought over so much fluoride of silicon that the contents of the tube are semi-solid, and nearly the whole of it has passed over. The temperature is then raised to 150° C., and the retort allowed to cool. The process is next repeated with a fresh charge of acid and ammonia. If no more than 0·2 grm. of silicate be taken, twice charging of the retort is sufficient; but with 0·5 grm., three or four repetitions of the process are required. In short, the operation is continued, with fresh reagents, till no more flock of silica forms in the receiver. Finally, 0·75 c.c. of sulphuric acid is introduced into the retort, and the temperature again raised to 160° C., the stream of hydrogen being continued as before.

The several ammoniacal charges are poured into a platinum dish, together with the washings of the delivery-tube and the two test-tubes, and slowly evaporated in a water-bath with continued stirring.

At a point in the evaporation, just before the solution becomes neutral, and the fluoride of ammonium begins to turn acid, the entire silica in the dish will have been dissolved by the fluoride. The process is gradual, but the moment when the solution is complete is easily determined. Then, the dish being removed, chloride of potassium is added in slight excess, together with absolute alcohol equal in volume to the contents of the platinum vessel. Fluosilicate of potassium precipitates, which, after the lapse of twenty-four hours, is filtered, washed with a mixture of equal volumes of absolute alcohol and water, dried, and weighed. The results are accurate. In the retort are the bases in the form of sulphates, the treatment of which calls for no further remark.

Decomposition of Silicates in the Dry Way.

A. By Hydrofluoric Acid at a Red Heat.—M. F. Kuhlmann treats silicates at a dull red heat with a current of hydrofluoric acid. The apparatus for this process consists of a platinum retort, of which the belly may be of lead; the acid is produced in it by means of sulphuric acid and white cryolite, or pure fluoride of calcium. The neck of the retort fits tightly into a tube of platinum, which contains, in boats of the same metal, the matter to be analysed; this tube, by means of a short adapter, also of platinum, communicates with a condensing or absorbing apparatus; this apparatus may be of vulcanised india-rubber. One hour's heating suffices for the treatment of 10 grms. of mineral, but not more than 2 grms. should be employed.

B. By Fusion with a Fluoride.—Dr. Vorwerk recommends that one part of the very finely powdered mineral should be mixed with three parts of fluoride of sodium, and that this mixture, after having been placed in a platinum crucible, should be covered with 12 parts of powdered bisulphate of potassium, and the whole raised to a red heat. Not only are silicates readily decomposed in this manner, but such minerals as chrome-iron ore, hard hæmatite, tin ores, rutile, corundum, &c., are very readily brought to fusion and disintegrated by this flux, even with no more heat than that obtained from a good Bunsen gas burner.

C. By Fusion with Carbonate of Calcium and Sal-Ammoniac.—In chap. 1, p. 18, will be found a description of Professor J. Lawrence Smith's method of separating the alkalies from silicates. Since the original publication of that process Professor Smith has made numerous improvements in it, and he has within the last few weeks favoured the writer with a very detailed account of his most recent method, hitherto unpublished,

of attacking silicates for the purpose of separating the alkalies. Had this description been available at the time the first chapter was passing through the press, it would probably have supplemented, or possibly replaced, the process there given, and have fallen into its place in the chapter on alkali metals. Not being, however, at our disposal until very recently, we have no choice but to let it appear under the slightly less appropriate heading of "Silicates." The great value of the analytical process now printed for the first time will, it is trusted, be considered a sufficient excuse for the slight sacrifice of methodical arrangement which its publication here necessitates. We prefer to give Professor Smith's description in his own words.

1. In this description of separating and determining the alkalies, it is my intention to give the minutest details, although it may be thought useless by some; but numerous analyses have given me the experience here detailed; and I am convinced that analytical chemists, if they follow them out, will never resort to any other known method after a few trials; and if there be a better method, it is yet to be discovered. The presence of boracic, hydrofluoric, and phosphoric acids in the minerals in no way interferes with the process. Even in silicates *soluble in acids*, I prefer this method, in common with other analysts, for its ease and accuracy.

2. During the latter part of 1852 I made the researches, the details of which were published early in 1853.* Since that time I have employed the process many hundreds of times with the greatest satisfaction, most accurate results, and ready manipulation; some minor points were not completed satisfactorily until several years after the first notice of the method; these have been subsequently perfected, and in my mind there is nothing further now to be desired. I might state that many analytical chemists have for years constantly used this process to the exclusion of all others.

3. The purpose of this article is to give all the perfections, and a minute detail of the manipulations, with whatever precautions are necessary, all of which are simple and easily executed. In the two articles on the subject of alkali determination in minerals, published in 1853, the whole subject was reviewed, which is needless to recur to now. I then reviewed the process by caustic baryta and its salts, by hydrofluoric acid, also detailing some experiments on the separation of the different alkalies from each other, microscopic examinations of the same, &c. It was shown that after the caustic alkalies, the most powerful agent to attack silicates at a high temperature is caustic lime, a fact not new to chemists, for as early as 1847 I used this process for attacking silicates, and others had done the same prior to that period. But for the purpose of arriving conveniently at

* Shortly after my first publication, M. St. Claire Deville made known his method of analysing the silicates by *fusion* with lime; but the nature of his process and the objects to be arrived at were quite different from those attained by the process under consideration.

a quantitative determination of the alkalies in silicates, certain methods of manipulation, quantity of material, admixture, &c., had to be discovered, and in them resides the success of my process—converting the most difficult parts of the analysis of a silicate into the easiest.

4. The methods of analysis of the silicates by caustic baryta and its carbonate are well known; but for various reasons fully detailed by Rose, in his "Analytical Chemistry," are now no longer used. The method still employed extensively is the one proposed by Berzelius, with hydrofluoric acids, and when applied with numerous precautions, it seems to decompose all silicates; still, according to Rose, there are siliceous compounds that cannot be completely decomposed by hydrofluoric acid.* Dismissing all criticism, I at once proceed to the method which is the subject of this article.

5. **Decomposition of Silicates by Ignition with Carbonate of Lime and Sal-Ammoniac.**—This mixture of carbonate of lime and sal-ammoniac is used simply for the purpose of bringing in a most thorough manner caustic lime to act upon the silicates at a red heat.† The first step in the process is to have pure *carbonate of lime*.

6. This is made in my laboratory as follows:—Take as good marble as can be conveniently found (not dolomitic), or calc spar, and dissolve in hydrochloric acid. (It is not necessary that the acid be perfectly pure). Add an excess of the marble and warm the solution; to it add lime-water or some milk of lime, made from pure or nearly pure lime, until the solution is alkaline to test-paper; the lime is added to precipitate any magnesia, phosphate of lime, &c., that may have been in the marble. Filter this solution, and after heating it to at least 160° F., precipitate with carbonate of ammonia.‡ The carbonate of lime thus precipitated is to be thrown on a filter and well washed with pure rain-water or with distilled water.

7. Thus prepared, the carbonate of lime is a dense powder and perfectly pure; or, if it contain any impurity, it will be a trace of carbonate of baryta or strontia, which in no way interferes with the use of the carbonate of lime.

* The process used by Deville in fusing with lime is in most cases better than that by hydrofluoric acid, and one that I should use in preference to all others, except the one now being described.

† Chloride of calcium at a red heat will dissolve more or less caustic lime.

‡ This precaution must not be overlooked, as it is desirable to obtain the precipitated carbonate of lime as dense as possible. If the carbonate of ammonia be added to the cold solution, the precipitate, at first gelatinous, will ultimately become much more dense and settle readily; the same is true if the mixture be heated after the addition of the carbonate of ammonia; but in neither case will it be as dense as when the carbonate is added to the hot solution of chloride of calcium. The reaction in this process of analysis is in no way effected by the form of the carbonate of lime; but by using the denser form, the mixture occupies less space in the crucible in which it is heated.

8. **Sal-Ammoniac.**—To give to this reagent the most convenient form, take fragments of clean sublimed sal-ammoniac, dissolve them in water over a gentle fire, filter, evaporate the filtered solution over a steam-bath, or on a sand-bath, or any other convenient gentle heat, and as the small crystals deposit themselves, stir the solution to keep the crystals small; when one-half or two-thirds of the sal-ammoniac is deposited, pour off the liquid without waiting for it to cool, throw on a cotton filter, and dry the crystals at the temperature of the atmosphere. In this way, sal-ammoniac is furnished that is easily pulverised.

9. **Vessels for Producing the Decomposition.**—The ordinary platinum crucible can be employed for this purpose, and is now most commonly used, and for many years was used by myself. It is, however, found that, while this method exceeds in precision and ease all other known methods for alkali determinations in silicates, there was yet a very minute quantity of alkalies lost by volatilisation, and while the method gave satisfaction to those who used it, I yet continued my researches to overcome even this small loss. This has been successfully accomplished, and for some time I have been in the constant habit of using an improved form. Instead of the ordinary platinum crucible, I use an elongated one, which may be made of various dimensions. The one employed, with from ½ to 1 grm. of silicate, is of the following form and dimensions.

10. An elongated slightly conical crucible with rounded bottom, and having a cover with or without a central wire to hold the cover; its length is 95 millimetres; diameter of opening 22 millimetres; diameter of small end, just at the turn of the bottom, 16 millimetres; and weighs about 35 or 40 grms. It can be made lighter, but experience has shown that it is better if stiff and solid. Messrs. Johnson and Matthey, Hatton Garden, London, have made a number for me, and they have my drawings and directions. It is thus made for the purpose of having that portion of the crucible containing the mixture heated strongly, while the upper portion is below a red heat.

11. **Manner of Heating the Crucible.**—If the ordinary crucible be used, it is heated in the manner usually employed for the fusion of silicates. If the new form of crucible be employed, then the upper part may be grasped by a convenient metallic clamp in a slightly inclined position, and a moderate blast from the table blowpipe made to play upon it for about 25 or 30 minutes. But now gas is to be found in every well-mounted laboratory, Bunsen burners of all dimensions are used, and when properly applied, can be made to give gradations of heat, from the mildest to that sufficient to melt cast-iron. A simple, cheap, and convenient furnace, with a properly arranged draft, can be made to accomplish all silicate fusions without the aid of any manual labour, and therefore I employ such an

apparatus, of which a description will be given at the end of this article.

12. **Method of Analysis.**—We have now the pure carbonate of lime, granular sal-ammoniac, and the proper crucible. The silicate is to be well pulverised in an agate mortar;* for the analysis I take ½ grm. or 1 grm., the former is most commonly used, as being sufficient, and best manipulated in the crucible used; a gramme, however, may be conveniently employed. The weighed mineral is placed in a large agate mortar, or better in a glazed porcelain mortar of ½ to 1 pint capacity. Weigh out an equal quantity of the granular sal-ammoniac (a centigramme more or less is of no consequence), put it in the mortar with the mineral, rub the two together intimately; after which add 8 parts of carbonate of lime in three or four portions, and mix intimately after each addition; empty the contents of the mortar completely upon a piece of glazed paper, that ought always to be under the mortar, and introduce into the crucible. The crucible is tapped gently upon the table and the contents settled down.

13. It is then clasped by a metallic clamp in an inclined position, or it is placed in the support referred to in the latter part of this article, leaving outside about ½ or ¾ inch; a small Bunsen burner is now placed beneath the crucible, and the heat brought to bear just about the top of the mixture, and gradually carried toward the lower part, until the sal-ammoniac is completely decomposed, which takes about 4 or 5 minutes; heat is then applied in the manner suggested, either with the blast or with the burners referred to, acting by its own draught, and the whole kept up to a bright red heat, for about from 40 to 60 minutes. It is well to avoid too intense a heat, as it may vitrify the mass too much.

14. The crucible is now allowed to cool, and, when cold, the contents will be found to be more or less agglomerated in the form of a semi-fused mass; a glass rod or blunt steel point will most commonly detach the mass, which is to be dropped into a platinum or porcelain capsule of about 150 c.c. capacity and 60 or 80 c.c. of distilled water is added. In the course of a longer or shorter space of time, the mass will slake and crumble after the manner of lime; still better, this may be hastened by bringing the contents of the capsule to the boiling point, either over a lamp or water-bath. At the same time, water is put into the crucible to slake out any small particles that may adhere to it, and subsequently this is added to that in the capsule, *washing off the cover of the crucible also.*

* While in all mineral analyses, thorough pulverisation of the mineral is usually essential, still it is a singular fact that very good analyses can be made with this method, even when the powder is tolerably coarse, and in some experiments with lepidolite, powder was used with much of it in particles from 1-40th to 1-30th of an inch in size, giving good results. Notwithstanding this, thorough trituration of the mineral is recommended.

15. After the mass is completely slaked, the analysis may be proceeded with, although, as a general thing, I prefer to allow the digestion to continue six or eight hours, which, however, is not necessary. If the contents of the crucible are not easily detached, do not use unnecessary force, as the crucible may be injured by it, but fill the crucible to about two-thirds of its capacity with water, bring almost to the boiling point, and lay it in the capsule, with the upper portion resting on the edge; the lime will slake in the crucible, and then may be washed thoroughly into the dish, and, as before, the cover is to be washed off.

16. We have now by this treatment with water the excess of lime slaked into a hydrate, and some of the lime, combined with the silica and other ingredients of the silicate, in an impalpable form; in solution there is the excess of the chloride of calcium formed in the operation, and all the alkalies originally contained in the mineral as chlorides, and all that now remains to be done is to filter, separate the lime as carbonate, and we have nothing left but the chlorides of the alkalies. To do this, I proceed as follows:—

17. Throw the contents of the capsule on a filter (the size preferred for the quantity above specified is one 3 to 3½ inches in diameter), wash well, to do which requires about 200 c.c. of water; the washing is executed rapidly. The contents of the filter (except in those cases where the amount of the mineral is very small, and there is no more for the estimation of the other constituents) is of no use, unless it be desired to heat again, first adding a little sal-ammoniac to see if any alkali still remains in it, a precaution I find unnecessary. The filtrate contains in solution all the alkalies of the mineral, together with some chloride of calcium and caustic lime; to this solution, after it has been placed in a platinum or porcelain capsule, is added a solution of pure carbonate of ammonia; (equal to about 1½ grms. is required).

18. This precipitates all the lime as carbonate; it is not, however, filtered immediately, but is evaporated over a water-bath to about 40 c. centimetres, and to this we add again a little carbonate of ammonia and a few drops of caustic-ammonia to precipitate a little lime that is re-dissolved by the action of the sal-ammoniac on the carbonate of lime. Filter on a small filter (2 inches), which is readily and thoroughly washed with but a little water, and the filtrate allowed to run into a small beaker glass. In this filtrate are all the alkalies as chlorides and a little sal-ammoniac; add a drop of a solution of carbonate of ammonia, to make sure that no lime is present. Evaporate over a water-bath in a tared platinum dish, in which the alkalies are to be weighed; the capsule used is about from 30 to 60 c. centimetres capacity, and during the evaporation is never filled to more than two-thirds its capacity.

19. After the filtrate has been evaporated over the water-bath to dryness, the bottom of the dish is dried, and on a proper support heated *very gently* by a Bunsen flame to drive off the little sal-ammoniac. It is well to cover the capsule with a piece of thin platinum to prevent any possible loss by the spitting of the salt after the sal-ammoniac has been driven off. Gradually increasing the heat, the temperature of the dish is brought up to a point a little below redness, the cover being off (the cover can be cleansed from any sal-ammoniac that may have condensed by heating it over the lamp). The capsule is again covered, and when sufficiently cooled, before becoming fully cold, is placed on the balance and weighed. This weight gives as chlorides the amount of alkalies contained in the mineral.

20. If chloride of lithium be present, it is necessary to weigh quickly, for this salt being very deliquescent attracts moisture rapidly.

It not unfrequently occurs that the chlorides at the end of the analysis are more or less coloured with a small amount of carbon, arising from certain constituents in carbonate of ammonia; the quantity is usually very minute, and in no way affects the accuracy of the analysis. In selecting pure carbonate of ammonia for analytical purposes, it is well to select specimens that are not coloured by the action of the light.

21. It only now remains to separate the alkali by the known methods. Under this head I have made several observations that will be published as soon as they are considered satisfactory.

22. **A Special Arrangement for Heating the Crucibles by Gas.**—The support and burner, where gas is to be had (as it is in almost all analytical laboratories) are simple in their character, and have been arrived at after a great variety of experiments with gas furnaces. The figure here given illustrates the stand, burner, crucible, &c., and is about one-sixth the natural size. H is the stand with its rod, G. D is a brass clamp, with two holes at right angle to each other; having two binding screws, it slides on the rod, G; the second hole is for a round arm attached to B, the binding screw, E, fixing it in any position. B is a plate of cast-iron, 5 to 6 millimetres thick, 10 to 11 centimetres long, and 4½ centimetres broad, having a hole in its centre large enough to admit the crucible to within about 15 millimetres of the cover without binding. A is the crucible already referred to, which is made to incline a few degrees downwards, by turning the plate of iron that supports it. C is a chimney of sheet iron, 8 to 9 centimetres long, 10 centimetres high, the width at the bottom being about 4 centimetres at one end, and about 3 centimetres at the other end. It is made with the sides straight for about 4 centimetres, then inclines towards the top, so as leave the width of the opening at the top about 1 centimetre. A piece is cut out of the front of the chimney of the width of the diameter of the hole in the iron support, and about 4 centimetres in length, being

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within 2 or 3 per cent in one hour, and when mixed with silica or a silicate, in a very much shorter space of time, although in my analyses I employ one hour, as it requires no attention after the operation is once started. This form of furnace and crucible is found to be convenient for other operations.

24. Although the details given here are lengthy, the time occupied in the analysis is short and the precautions necessary are of a simple character, so much so that results obtained by students on beginning chemical analysis have been found by me reliable, and less variable on the alkalies of the silicates than of any of the other constituents of this class of bodies. I have often made good alkali determinations in three hours from the commencement of the operations, hastening the evaporations by more direct application of heat, which, of course, requires close watching.

25. It is a common practice, when a silicate comes under my examination that is not easily made out by its physical properties, to make at once an alkali determination, which often indicates at once what it is if it be a known silicate. If not, the alkali determination serves as one step in its examination.

CHAPTER XIV.

GENERAL ANALYTICAL PROCESSES.

GAS ANALYSIS.*

I. Analysis of a Mixture of Oxygen, Carbonic Acid, and Nitrogen.

1. Introduce a portion of the mixture into a graduated tube over mercury, and note accurately the volume.

To estimate the carbonic acid, pass into the tube, by means of a curved pipette, a small quantity of a concentrated solution of potash, and agitate several times until there is no further variation in the level of the liquid; the carbonic acid will be absorbed by the potash. To obtain the volume very accurately, transfer the gas to a vessel of water so as to allow the alkali to fall out; then re-transfer the gas to another tube and determine its volume, saturated with moisture.

To estimate the oxygen, first introduce into the tube a concentrated solution of potash, then a little pyrogallic acid. Upon agitation, the oxygen is absorbed, and the nitrogen remains. The bulk of the latter gas may be obtained by taking the same precautions as in the former instance.

After having removed the carbonic acid, phosphorus may also be employed to absorb the oxygen. The experiment may be performed in two ways:—

a. In the Cold.—In the tube containing the gas (over mercury) pass up a long stick of moist phosphorus, the sides of the tube being at the same time moistened. The oxygen combines with the phosphorus, giving phosphorous acid, which dissolves in the water. At the end of an hour the absorption is completed. It may be known by the absence of white fumes on the stick of phosphorus. Remove the latter, dry the gas, and measure its volume; it will be nitrogen.

b. With Heat.—The analysis is effected much more rapidly in the following manner:—In a curved tube containing the mixture of oxygen and nitrogen standing over water, introduce by means of an iron wire a small piece of phosphorus, so that it rests in the upper curved portion of the tube;

* These methods are principally founded on instructions given by Drs. Grandeau and Troost.

then remove the iron wire and heat the phosphorus, at first carefully, to volatilise the water which remains in the bend of the tube, and then rapidly, so as to inflame the vapour of phosphorus. A greenish flame will be seen to advance, gradually absorbing the oxygen of the air. When it has descended to the level of the liquid it disappears, and the experiment is terminated. Allow it to cool, and determine the volume of the residual nitrogen.

2. The analysis of a mixture of carbonic acid, oxygen, and nitrogen may be effected with a little more accuracy in the following manner:—The dry mixture being contained in a graduated tube standing over mercury, introduce a piece of caustic potash fixed to the extremity of a platinum wire, and slightly moistened. When the carbonic acid is absorbed, withdraw the piece of potash, and a simple observation gives the residual volume of the mixed oxygen and nitrogen perfectly dry.

The residue is introduced into a mercurial eudiometer. This consists of a glass tube about 2 centimetres in diameter, having two platinum wires melted through the upper part, terminating exteriorly in a loop, and curved inside in such a manner as to have their extremities opposite to each other and one or two millimetres apart, across which the spark passes.

Add to the mixture double its volume of hydrogen, and pass the electric spark. Water will be produced by the combination of the hydrogen and oxygen in the proportion of two volumes of the former to one volume of the latter. One-third of the diminution in volume, therefore, represents the volume of oxygen. The volume of nitrogen is obtained by difference; it will be the excess of the original volume of the mixture over the sum of the volumes of oxygen and carbonic acid.

The estimation of oxygen by the eudiometer is not exact unless this gas is present in tolerable quantity in the mixture. If there is only a very small proportion, it is necessary, in order to ensure complete combustion, to take the precaution to introduce into the mixture a sufficiently large quantity of oxy-hydrogen gas, obtained by decomposing acidulated water with three or four Bunsen's elements. The gas should be passed through concentrated sulphuric acid in order to dry it.

II. Mixture of Oxygen, Hydrogen, and Nitrogen.

1. After having measured the volume of the mixture, absorb the oxygen by potash and pyrogallic acid, or by phosphorus as already described (I.).

Pass the remainder into a curved tube over mercury, and introduce into it a piece of compact oxide of copper,* and heat it for about twenty minutes,

* This oxide is prepared by fusing 2 parts of oxide of copper with 1 part of oxide of lead. The fused mass is run on to a plate of copper, then broken into pieces and preserved in bottles.

all the hydrogen is then absorbed; the residue will be nitrogen; it may be transferred to a graduated tube, and its volume measured.

After the absorption of the oxygen the hydrogen may be estimated by introducing it into the eudiometer with half its volume of oxygen. Two-thirds of the diminution of volume occasioned by the passage of the spark represents the volume of hydrogen. The nitrogen is given by difference.

2. The analysis may also be effected entirely by the eudiometer. Introduce the original mixture into the eudiometer with twice its volume of hydrogen, and pass the spark. The volume of hydrogen which enters into combination will be two-thirds the diminution of volume, the oxygen being represented by the other third. This first experiment will therefore give the amount of oxygen. In order to ascertain the amount of hydrogen in the mixture, add to the residue of the first explosion half its volume of oxygen, and pass the spark a second time. Two-thirds of the diminution of volume will be hydrogen. The excess of the sum of the volumes of hydrogen burnt in these two experiments, over the volume of this gas introduced into the eudiometer, represents the volume of hydrogen found in the original mixture. The nitrogen will still be given by difference.

III. Mixture of Hydrogen, Marsh Gas, and Nitrogen.

Introduce the mixture into a mercurial eudiometer with twice its volume of oxygen, and pass the spark. The free hydrogen and that in the marsh gas combine with the oxygen to form aqueous vapour, which condenses. The carbon becomes carbonic acid. The residue is therefore a mixture of nitrogen, oxygen, and carbonic acid.

Pass these gases into a graduated tube, and after having observed the volume, absorb the carbonic acid with potash. The diminution of volume gives the volume of carbonic acid, which will be equal to the volume of the carburetted hydrogen originally present.

If a little pyrogallic acid is then introduced into the potash, the rest of the oxygen is absorbed, and the volume of nitrogen is obtained as a residue.

The amount of the hydrogen which existed in the free state in the original mixture, is obtained by taking the excess of the volume of the original mixture over the sum of the volumes of nitrogen and marsh gas.

IV. Mixture of Sulphuretted Hydrogen, Carbonic Acid, and Nitrogen.

The mixture is measured into a graduated tube standing over mercury. Introduce a solution of sulphate of copper, and agitate. The diminution of volume represents the amount of sulphuretted hydrogen present.

Bunsen recommends in preference for the absorption of the sulphuretted hydrogen, a ball of binoxide of manganese impregnated with phosphoric

acid. [To obtain a ball of binoxide of manganese which does not tend by reason of its porosity to absorb other gases besides sulphuretted hydrogen, Bunsen prepares by levigation a fine powder, which is formed into a thick paste by a little water. This paste is then pressed into a mould round a platinum wire, the extremity of which is twisted into a spiral. The mould is then dried at a gentle heat, when the ball of binoxide is readily detached; for greater precaution, the sides of the mould may be smeared with a little oil. The ball is then moistened several times with a syrupy solution of phosphoric acid].

The remaining gas, transferred to an appropriate tube, is then submitted to the action of caustic potash, which absorbs the carbonic acid. The residue is nitrogen.

V. Mixture of Hydrochloric Acid, Sulphuretted Hydrogen, Carbonic Acid, and Nitrogen.

When the exact volume of the mixture has been accurately measured in a tube over the mercury, the hydrochloric acid is absorbed by a fragment of hydrated sulphate of sodium fixed to the extremity of a platinum wire. [To obtain these fragments fuse ordinary sulphate of sodium in its water of crystallisation, and dip in several times the end of a platinum wire. There adheres to the wire a small lump of the sulphate, which augments in volume with each fresh immersion].

Then remove the sulphate of sodium, and measure the volume again. The diminution observed will represent the volume of hydrochloric acid gas.

The sulphuretted hydrogen is absorbed by a ball of binoxide of manganese soaked in phosphoric acid, and the carbonic acid is afterwards absorbed by potash. The residue gives the nitrogen.

VI. Mixture of Sulphurous Acid, Carbonic Acid, Oxygen, and Nitrogen.

(Gas issuing from Craters of Solfatara.)

The volume of the mixture being measured dry in a graduated tube over mercury, the sulphurous acid is absorbed by a ball of binoxide of manganese impregnated with phosphoric acid. After having removed this ball and noted the diminution of volume, a fragment of potash is introduced to absorb the carbonic acid. The second diminution of volume will give the carbonic acid.

The oxygen can then be absorbed by potash and pyrogallic acid; or it may be estimated eudiometrically as described in No. 1. The nitrogen will remain as residue.

VII. Sulphuretted Hydrogen, Carbonic Acid, Hydrogen, and Nitrogen.

(Fumeroles of Volcanoes.)

Commence by absorbing the sulphuretted hydrogen by introducing into the mixture a ball of binoxide of manganese impregnated with phosphoric acid. The absorption of the carbonic acid is then effected by means of a fragment of moist caustic potash.

The hydrogen is then estimated as in No. 2, either by the eudiometer, or by passing the mixture of hydrogen and nitrogen into a curved tube and introducing compact oxide of copper into the upper part of the bend. By heating the part of the tube containing this oxide for a quarter of an hour, the complete absorption of the hydrogen is effected. The nitrogen will form the residue.

VIII. Carbonic Acid, Carbonic Oxide, Hydrogen, and Nitrogen.

(Gas from Blast Furnaces where Wood is used.)

After having accurately measured the volume of the mixture over mercury, absorb the carbonic acid with a fragment of caustic potash.

Then estimate the carbonic oxide by introducing into the graduated tube a solution of subchloride of copper in hydrochloric acid, agitate, and the absorption will be complete.

Instead of introducing the liquid itself, it will be better, as Bunsen advises, to introduce a ball of papier maché impregnated with this acid solution of subchloride of copper.

This experiment should be made over another separate mercurial trough, for the subchloride of copper attacks and fouls the mercury.

In withdrawing the ball impregnated with chloride, before reading off the volume, it is necessary to remove the hydrochloric acid vapours given off by the chloride.

The estimation of the hydrogen can then be effected as in No. 2, either by the eudiometer or by absorption with oxide of copper. The nitrogen remains as a residue.

IX. Carbonic Acid, Carbonic Oxide, Hydrogen, Marsh Gas, Nitrogen.

(Gas from the Mud of a Pond.)

First estimate the carbonic acid by means of potash, then with a ball of papier maché introduce into the mixture a concentrated solution of subchloride of copper in hydrochloric acid. After the absorption has terminated, withdraw the ball of chloride and replace it by a ball of potash to remove the vapours of hydrochloric acid given off by the acid chloride. If the mixture which contains carbonic oxide also contains oxygen, the latter gas

is determined first by pyrogallic acid and potash. The estimation of the hydrogen and marsh gas is then effected eudiometrically as in No. 3.

X. Sulphuretted Hydrogen, Carbonic Acid, Carbonic Oxide, Olefiant Gas, Marsh Gas, Hydrogen, Nitrogen.

(Coal Gas.)

The mixture is first accurately measured in a graduated tube standing over mercury. The sulphuretted hydrogen is then estimated by means of a ball of binoxide of manganese impregnated with phosphoric acid.

After removing the binoxide of manganese and measuring the remaining volume, introduce a ball of caustic potash, which absorbs carbonic acid.

The carbonic oxide is determined by means of acid subchloride of copper.

To determine the olefiant gas introduce into the residue a fragment of coke soaked in a concentrated solution of anhydrous sulphuric acid in monohydrated sulphuric acid. The absorption of the olefiant gas takes place very rapidly; the coke is then withdrawn and the acid vapours absorbed by potash.

The estimation of the hydrogen and marsh gas is then performed as in No. 3. The nitrogen remains as a residue.

The olefiant gas, as well as the marsh gas and the hydrogen, may also be estimated by the eudiometer. To effect this pass the mixture of these three gases and the nitrogen into the eudiometer with three times its volume of oxygen, and pass the spark. The free hydrogen, as well as that of the carburets, combine with oxygen to form water, whilst the carbon becomes carbonic acid. Then pass the residue of the combustion into a graduated tube, and estimate the carbonic acid with potash, and the excess of oxygen with potash and pyrogallic acid. The residue left after this double absorption gives the nitrogen.

The volumes of olefiant gas, marsh gas, and hydrogen may then be obtained by a simple calculation. The reactions which take place show:—
1. That the combustion of olefiant gas requires thrice its volume of oxygen, that of marsh gas double its volume, and that of hydrogen half only.
2. That the olefiant gas produces double its volume of carbonic acid, and the marsh gas its own volume exactly.

Therefore, calling x, y, z the volumes of the olefiant gas, the marsh gas, and the free hydrogen, of which the sum is known and represented by c, we have—

$$3x+2y+\frac{z}{2}=a$$
$$2x+y=b$$
$$x+y+z=c$$

a and b are the volumes of oxygen employed, and of the carbonic acid produced, volumes which have been determined by experiment.

To find the values of x, y, and z, subtracting the first equation from the sum of the two others, we find—

$$\frac{z}{2} = c+b-a, \text{ whence } z=2(b+c-a),$$

Then subtracting the last from the second we find—

$$x-2(b+c-a)=b-c, \text{ whence } x=3b+c-2a,$$

The second equation then gives—

$$y=4a-5b-2c.$$

VOLUMETRIC ANALYSIS.

Standard Solutions of Acid and Alkali.

In the greater number of analytical examinations of free acids and alkalies the rule is to employ a normal acid, and a normal solution of caustic alkali, and also a tenfold dilution of them (1-10th of the normal liquids). In choosing the most appropriate acid for this purpose, it must be taken into consideration that it should form with alkaline or earthy metals only soluble salts, in order that the change of colour in the liquid under examination—which is coloured with litmus—may not be interfered with by precipitates, and also that the carbonic acid may be perfectly displaced by the normal acid.

Dr. Fleischer strongly advises that hydrochloric acid should be used as the standard acid, instead of nitric, sulphuric, or oxalic acid. It is as appropriate a standard acid as nitric acid, is more easily obtained pure, and is more constant to one standard. Another advantage possessed by hydrochloric acid is, that the acid contained in it may be not only estimated alkalimetrically, but also quickly and exactly, by a standard silver solution, a test which is impossible in the case of nitric acid.

With regard to volatility, it may be mentioned that hydrochloric acid, diluted to one-fifth of the normal strength, when heated for ten minutes, replacing the water as it evaporates, will not impart the slightest tinge of red to a blue litmus paper held in the vapours evolved, and, as in alkalimetric investigations the dilution is much greater, there need be no fear of driving off the free acid by digestion. Moreover, the constancy of normal hydrochloric acid is so great, that, after keeping for months, the change can scarcely be perceived, provided it has been preserved in well-stoppered bottles.

The next important standard solution for analysis by saturation is caustic alkali. The difficulty of preserving either caustic potash or soda free from

carbonic acid for any length of time is very great, and in the endeavour to secure this end complicated and inconvenient systems of syphons and tubes are sometimes connected with the stock bottle.

All these inconveniences, which exert more or less influence upon the accuracy of estimation, may, however, be remedied by employing, instead of the normal potash or soda solution, caustic ammonia of half the normal strength. Of all caustic solutions, caustic ammonia displays the most complete indifference to carbonic acid; so complete, in fact, that a flask partly filled with half-normal ammonia, well closed with a glass stopper, and which was frequently opened for estimations to be made, gave no indications of carbonic acid after three months' preservation. Moreover, the standard of this half normal liquid was so slightly altered during the three months, that 1-10th c.c. of a tested normal hydrochloric acid was scarcely perceptibly less saturated by 50 c.c. of it than it would have been had it been theoretically accurate.

It follows from these experiments that the half-normal ammonia liquid is at least as useful in acidimetrical work as the best caustic potash solution; besides which, ammonia has the advantage of being conveniently preserved, and of being easily obtainable chemically pure.

With respect to the blue colouration of litmus in a liquid previously reddened by free acid, so as to fix the final reaction in analysis by saturation, the following is worthy of remark:—

Cold dilute solutions of neutral sulphate or nitrate of ammonium scarcely produce any perceptible change in blue litmus solution—at any rate, much less than that produced by the introduction of two bubbles of carbonic acid. Sal-ammoniac, under these circumstances, appears perfectly neutral, and a single drop of half-normal ammonia produces in these litmus-coloured solutions a strong and lasting blue colour, slightly inclining towards violet.

Hot solutions of the ammoniacal salts in question, and especially sulphate of ammonium, act upon litmus in a somewhat acid manner, about the same as free carbonic acid; whence it follows that, in all estimations by ammonia, the liquid to be tested should be cold. If previously heated, it should be cooled as much as possible by immersion in cold water. If this be attended to, the distinctness of the tint will leave nothing to be desired. The objection may be raised, that ammonia cannot be employed, like potash or soda, as a normal, but only as a half-normal, liquid; the relation of the base to the acid as 2 : 1 is, however, more advantageous to the exactness of the determination than if both fluids possessed the same equivalents.

The standard of the normal hydrochloric acid liquid is ascertained by a weighed amount of pure carbonate of calcium slightly heated. The best way to preserve both liquids is in well-closed bottles, with glass stoppers. They should be placed in a cool place, free from dust. In hot summer

weather, the bottle containing the half-normal ammonia should be placed in cold water, renewed daily, as there is danger of a long-continued high temperature altering its standard, though only in a slight degree.

A New General Method of Volumetric Analysis.

H. Rose has suggested that in particular cases the heavy metal in nitrates might be precipitated by means of sulphuretted hydrogen, and the nitric acid set free determined in the filtrate by volumetric methods. Wolcott Gibbs has generalised this method so as to form the basis of a new application of the processes of acidimetry. When the salt to be analysed contains a fixed acid which does not act upon sulphuretted hydrogen, a weighed portion is to be dissolved in water, the solution brought to a boiling heat, and a current of sulphuretted hydrogen passed through until the metal is completely precipitated. When quantities of about 5 grms. are employed the precipitation is usually complete in half an hour. The precipitate may then be allowed to settle, and a drop of the supernatant liquid taken out with a glass rod, and tested upon a white porcelain plate, with a drop of saturated solution of sulphuretted hydrogen in water, or with any other reagent which may be specially adapted to the metal in the salt examined. The precipitation being complete the liquid is filtered upon a ribbed filter, the filtrate and the washings allowed to flow into a half litre or litre measure, and the washing with hot water continued until a drop of the filtrate no longer exhibits an acid reaction. The liquid is then allowed to cool, and the volume made up to exactly a half litre or litre by the addition of water. After thoroughly mixing the contents of the measure, 50 or 100 c.c. are to be taken out, a few drops of a solution of cochineal or logwood added, and the free acid determined by means of one-tenth normal ammonia in the usual manner. The first determination is to be used simply as a guide. Two or more successive portions of the acid liquid may then be taken out and determined successively, and the mean of several determinations obtained. With very little practice the results will be found to correspond to one-tenth c.c. when a burette with Erdmann's float is employed. From the quantity of ammonia required to neutralise the acid, the quantity of acid, and in many cases also of base, in the salt, may be readily calculated.

With crystallised sulphate of copper the following results were obtained:—

	Theory.		Experiment.	
		I.	II.	III.
CuO	31·86 ..	31·70	31·93	31·89
SO_3, ...	32·07 ..	31·89	32·14	32·10

In Rose's memoir he points out the necessity of diluting the solutions of

metallic nitrates to such a degree that the nitric acid set free shall not act sensibly upon the sulphuretted hydrogen.

In the experiments made to test the method this precaution was not found to be sufficient. Even dilute nitric acid acts too powerfully upon sulphuretted hydrogen to permit a very accurate determination of the former under the circumstances of the experiment. Precipitation from a boiling solution is necessary because the filtrate is then at once free from sulphuretted hydrogen.

To obviate the difficulty arising in the case of nitric acid, Dr. W. Gibbs recommends the addition to the solution of the nitrate of a portion of a neutral salt containing fixed organic acid, an equivalent quantity of which will be set free by the combination of the free nitric acid with the base contained in the salt. This method is found to give perfectly satisfactory results, Rochelle salt being usually added.

When chlorine is separated in the form of hydrochloric acid the volatilisation of the acid in the process of boiling is completely avoided by the addition of the organic salt. The same remark applies to nitric acid, though it is probable that the principal cause of loss in this case is the action of the acid at a boiling heat upon the gas passed through the liquid. The precipitation of a metal by sulphuretted hydrogen is usually much slower when boiling solutions are employed.

Under favourable circumstances, this method is capable of giving very satisfactory results. It is easy to see that it applies in the case of soluble definite compounds of all those metals which are easily and completely precipitated from boiling solutions by means of sulphuretted hydrogen. When the compound to be analysed contains an excess of free acid, not combined with the oxide of the metal to be determined, this must be first separated by evaporation to dryness in the usual manner. The presence of alkalies and alkaline earths is of course without influence on the result, but, on the other hand, even very small quantities of iron, aluminium, and various other bases, make it almost impossible to determine the point of saturation with precision, these metals in solution giving, with cochineal and logwood, specific reactions not easily distinguished from those produced by the alkalies in excess. For this reason the method does not apply when oxides of this class are present, and this case is precisely that which most frequently occurs in practice. The method will be applicable to all these cases if hereafter a colouring matter should be discovered sensitive only to acids or bases in excess, but not producing specific colouration with salts which are neutral in constitution. It is possible that cyanin, the remarkable properties of which have been described by Schönbein, or the rosocyanin of Schlumberger, may fulfil the condition indicated.

The method of precipitation here described may be used with advantage

in preparing a pure normal acid for titration. Pure crystallised sulphate of copper is to be powdered and heated in a porcelain crucible placed within a Hessian crucible for about an hour, the temperature being gradually raised and not allowed to exceed a low red heat. The anhydrous sulphate is then, while still hot, to be transferred to a perfectly dry glass tube, which can be closed with a good cork covered with tin foil. After cooling, the tube is weighed, the contents poured into a flask, the salt dissolved in water, and the copper precipitated at a boiling heat as above. The filtrate and washings are then to be made up to a known volume. From the weight of the anhydrous sulphate employed, the quantity of sulphuric acid present in the solution is known.

Generalisation of the Acidimetric Method.

M. Bunsen has proposed an acidimetric method which admits of estimating, by standard solutions, acids combined with the bases which are completely precipitated by caustic or carbonated alkalies. This method consists in adding an excess of the alkaline standard liquid to the solution of the salt, separating the precipitate by filtration, and determining the excess of alkali in the liquid by means of an acid liquid of a known standard.

The results obtained are in general very close to those required by theory.

A New Principle in Volumetric Analysis.

Dr. Mohr, of Coblentz, some time ago propounded a problem in volumetric analysis, and invited those interested in the subject to solve it. The problem was—"To perform quantitative determinations without the use of weights, with volumetric solutions of unknown strength, and the strength of which must not be ascertained and regulated."

The problem was first solved by Dr. Pauli in the following way:—In one of the pans of a balance is put a piece of chemically-pure carbonate of sodium, and in the other an equal weight of an undetermined soda, and both are measured by an acid of unknown strength. Suppose that in the first case 15 c.c., and in the second 11 c.c. have beed used, then

$$15 : 11 :: 100 : 73{\cdot}33.$$

The soda, therefore, contains 73·33 per cent carbonate of sodium.

The solution of the question, for which Dr. Pauli only cites a special case, is generally this:—

Equal portions of the pure substance to be determined and the impure are to be weighed off, one against the other, and are then to be measured with the same fluid; then the c.c. used for the pure substance represent 100 per cent, and the other number proportionately less. Suppose, for example, that it is proposed to determine the iron in an iron ore. A piece

of pure iron wire is placed in the scale of a balance, and is exactly counterpoised by means of the powdered ore; both are then brought into solution as protoxide in the usual way, and are then treated with permanganate of unknown strength. If oxide of iron is to be determined, pure oxide must be used instead of the wire. If potashes are to be examined, pure carbonate of potassium (recently heated to redness) should be used. It would appear from this, that for every analysis the strength must be determined by the pure substance. This, however, is easily avoided if we put a sixpence into the scale-pan, and weigh against this both the pure and impure substance. The number of c.c. of the fluid holds good as long as the same fluid and the same sixpence are used, and this number may be marked upon the bottle as expressing 100 per cent for the same substance.

This method is capable of universal application, and eliminates possible errors in weights and variations of temperature. It is only necessary that the substance to be determined should be available in the pure state.

But how is the problem to be solved, if it remains as before, but with the further condition, "when the substance to be determined is not available in a pure state?" Dr. Hiller solved the question, even with the condition that the pure substances should not be available, and in the same way as Dr. Mohr had already done it. For example,—if no chemically pure peroxide of manganese can be obtained for a manganese determination, pure permanganate, or pure bichromate of potassium, can be employed to weigh off the manganese; both are then converted by distillation with hydrochloric acid into chlorine, and then into iodine, and both fluids are then to be determined with the same unknown solution of hyposulphite of sodium. Instead of using pure permanganate, it would be better perhaps to use pure iodine to counterpoise the manganese, then to dissolve the iodine in iodide of potassium, and proceed as before. We have now to convert the value of the iodine into the value of an equal weight of pure peroxide of manganese, and express it in the c.c. of hyposulphite used. As 43·57 parts of binoxide of manganese set 127 parts of iodine at liberty, therefore any given weight of binoxide of manganese would set at liberty $\frac{127}{43.57}$, or 2·915 times as much iodine as is employed to counterbalance it. We have, therefore, to multiply the number of c.c. of hyposulphite which have been used for a quantity of iodine equal to the manganese by 2·915, and then to proceed as if pure binoxide of manganese and common manganese had been weighed together.

If pure carbonate of sodium cannot be obtained, pure carbonate of calcium may be used; the c.c. of the acid used must be multiplied by $\frac{50}{53}$, that is, 1 atom of carbonate of calcium divided by an atom of carbonate of sodium.

Improvements in the Process of Water Analysis.

When large quantities of an alkaline mineral water are evaporated in a porcelain dish, the saline matters, chiefly earthy carbonates, form a crust at the bottom of the vessel, so fixed that it is impossible to loosen it, while it need hardly be said that the residue cannot be weighed, while in the large basin, with accuracy. Dr. Mohr proposes to add to the water a sufficient quantity of formic acid, so as to render the fluid distinctly acid to test-paper, and then proceed with the evaporation cautiously, finishing it on a water-bath or in the drying-closet; the residue is dissolved in a small quantity of distilled water and the solution filtered through a small filter, the filtrate being run into a platinum crucible or basin of sufficient size, yet at the same time suitable for accurate weighing. The filter contains all the silica that was contained in the water, and, after washing and drying it, is readily estimated by well-known methods.

The filtrate in the platinum vessel is evaporated to dryness, and gently heated to redness; the formic acid does not, as acetic acid does, leave a carbonaceous residue, but is entirely converted into volatile compounds, viz., two atoms of carbonic oxide, and one atom of water; all the salts, therefore, which the mineral water contains are, after heating to redness, restored to the same condition they were in before the addition of the acid, and the residue, after weighing, is treated with boiling distilled water; this solution is filtered, and the insoluble residue on the filter treated by the well-known methods.

The soluble sodium-salts contain, or rather are combined with, carbonic and sulphuric acids and with chlorine; in order to estimate with the same quantity of substance each of these acids, Dr. Mohr suggests the following method:—The aqueous solution of the salts is boiled, and, while boiling, a neutral solution of acetate of calcium is added cautiously and drop by drop, so as to decompose the carbonate of sodium with the formation of carbonate of calcium in the form of arragonite; the carbonate of calcium is collected on a filter, and to the filtrate is added acetate of barium, while the fluid is kept in ebullition; the precipitated sulphate of barium is collected upon a filter, serving the purpose of the estimation of sulphuric acid; in the filtrate the chlorine is estimated by means of nitrate of silver, the solution having been acidified, previous to the addition of the solution of that salt, with nitric acid.

In this manner three different precipitates are obtained, from each of which the calculation for the corresponding sodium-salts is made. Carbonate of calcium $\times 1{\cdot}06 =$ carbonate of sodium $(\frac{53}{50} = 1{\cdot}06)$.

Volumetrically, the carbonate of sodium is first estimated with the aid of tincture of cochineal and 1-10th nitric acid; in the same fluid chlorine is volumetrically estimated by means of a solution of chromate of potassium,

and 1-10th nitrate of silver solution; after the addition of hydrochloric acid, the solution is filtered and the sulphuric acid in the filtrate is estimated gravimetrically by the ordinary method.

New Test for Reducing Agents.

Mr. Edwin Smith has published a method of illustrating the deoxidising property of sulphurous acid, by exposing a slip of bibulous paper, dipped in a mixed solution of sesquisulphate of iron and ferridcyanide of potassium, to the vapour rising from a bit of sulphur burning in air. The persalt of iron being reduced to a protosalt by giving up an equivalent of oxygen to the sulphurous acid, a blue reaction takes place with the ferridcyanide of potassium present in the solution. A solution of sulphurous acid, or of a sulphite or hyposulphite, gives the same result; while only a very slight greenish tinge is imparted to the mixture by a sulphate, except in the case of protosulphate of iron. With this exception, a useful test seems to be afforded between sulphites and sulphates. The same test will discriminate a nitrite from a nitrate.

To the mixed solution of sesquisulphate of iron and ferridcyanide of potassium add a few drops of nitric acid; then add a little of the solution to be tested. If the latter contains a nitrite, a greenish blue precipitate will begin to fall, and quickly increase; if a nitrate, only a slight greenish tinge will be imparted to the test. Nitric oxide or nitric trioxide passed into the mixed solution throws down the same characteristic precipitate, which is produced by the decomposition of a nitrite in the previous case. Carbonic oxide will act in the same way, and if a slip of paper dipped in the test-mixture be held over the clear part of a bright coal fire, it turns blue with the carbonic oxide or sulphurous acid there given off. Again, if a bit of phosphorus is dropped into a little of the test in a porcelain dish, the phosphorus immediately becomes coloured a greenish blue, and on stirring about, gradually imparts the same tinge to the solution. Phosphorous acid may be discriminated from phosphoric acid, just as sulphurous acid is distinguished from sulphuric acid by the blue reaction. Phosphites are also distinguished from phosphates. A solution of phosphorous acid shows the reaction readily on being shaken up with the test. Lastly, if copper turnings are boiled in the mixed solution for a few minutes, a greenish blue tint is imparted to it, which becomes gradually deeper with the oxidation of the copper and the consequent reduction of the persalt of iron to the state of a protosalt.

Improved Methods of Oxidation.

Professor Storer points out the superior oxidising power of a mixture of ordinary nitric acid and chlorate of potassium over that of the mixtures of

chlorate of potassium and hydrochloric or sulphuric acid commonly used in analysis.

Experience has shown not only that a mixture of nitric acid and chlorate of potassium oxidises more rapidly than the common mixture of hydrochloric acid and chlorate of potassium, but that it is really to be preferred, in the great majority of cases, to any of the agents ordinarily employed to effect oxidation in the wet way. Instead of occupying, as now, a secondary or alternative place in the treatises on analysis, it ought to take precedence of the other processes of oxidation. It may be used with advantage in many instances where dry methods of oxidation are now recommended. With the exception, perhaps, of the sulphides or other compounds of antimony and tin, there are probably but few cases where its use will be found inadmissible.

Estimation of Sulphur in Organic Compounds.

It is easy to determine sulphur in non-volatile organic compounds by oxidising the substance with chlorate of potassium and nitric acid, precipitating the sulphuric acid as sulphate of barium, and washing the latter with a solution of acetate of ammonium, to remove any nitrate of barium which may have adhered to it.

Mr. A. H. Pearson gives the following directions for carrying out the process:—To oxidise the sulphur compound, place a weighed quantity of it in a porcelain dish, pour upon it one or two ounces of strong nitric acid (39° B.), free from sulphuric acid, and add to the acid 30 or 40 grains of chlorate of potassium. Cover the mixture with an inverted glass funnel, the stem of which has been bent to a right angle. Place the dish on a wire gauze support and heat its contents. From time to time lift the funnel slightly and throw a small fragment of chlorate of potassium into the hot acid. The funnel must be of such a size that its rim may fall within the rim of the dish, and rest securely upon the sides of the dish above the liquid. It serves to retain the particles of liquid which are thrown up from the dish by the gas evolved during the decomposition of the chlorate.

The oxidation will be completed more or less rapidly, according to the character of the substance operated upon. Only five or ten minutes are required to completely oxidise a third of a grm. of sulphocyanide of potassium, while from half to three-quarters of an hour are needed to destroy the same weight of ordinary free sulphur. It may be observed, in passing, that sulphur which has just been distilled dissolves twice as rapidly in a mixture of nitric acid and chlorate of potassium as sulphur which has long been exposed to the air.

The foregoing method is not only applicable to the oxidation of sulphocyanide of potassium and free sulphur, as above described, but also for

estimating sulphur in vulcanised caoutchouc, and in samples of anthracite and bituminous coal. It is easy to completely oxidise either of these substances by means of the mixed chlorate of potassium and nitric acid. Anthracite dissolves even more readily than bituminous coal, since, unlike the latter, it does not fuse to a single mass in the hot acid.

Oxidation of Organic Matter in the Detection of Mineral Poisons.

In the oxidation of organic matter in substances supposed to contain mineral poisons, perhaps no process has been found to answer more perfectly than that in which the material is treated with powdered chlorate of potassium and hydrochloric acid. One serious objection to this process, however, arises from the large quantity of chloride of potassium necessarily produced by the decomposition of the chlorate of potassium by the hydrochloric acid, and the subsequent difficulties which have to be encountered, either from the crystallisation of this salt or from the quantity of water required for its solution. In order to overcome this difficulty, Mr. Glover has proposed the following modification of the process, which answers exceedingly well in practice. Introduce intó a large flask about 3 or 4 ozs. of chlorate of potassium, in crystals, as when the salt is powdered the action is too sudden. The flask is provided with a cork, through which pass two tubes, one a long funnel-tube to permit of the addition of hydrochloric acid from time to time, and the other bent twice at right angles, in the usual manner, so as to permit of the passage of the gas produced through the liquid to be operated upon. Now pour through the funnel-tube hydrochloric acid, of about the sp. gr. 1·05, that is, one part of the ordinary pure concentrated acid, and two parts of water. Heat is now applied to the flask, and the gases which come over are passed through the material which has to be oxidised, and which must be rendered liquid enough for the purpose by the addition of water. The process answers better if the beaker containing the liquids be removed between the renewals of the hydrochloric acid, when the gas has ceased to come off, and boiled. The funnel-tube, intended for the addition of the acid, serves likewise as a safety-tube, and must be made sufficiently long to prevent the column of liquid, which will be forced up some height in it by the pressure of the gas, from passing over at the top. This tube, likewise, by admitting atmospheric air at the proper time, prevents the liquid in the beaker from being carried back into the flask, an accident which is otherwise rather apt to happen towards the close of the disengagement of the gas.

Blowpipe Analysis. Employment of Chloride of Silver.

Amongst the phenomena which characterise different bodies before the blowpipe, and serve for their distinction, the colour of the flame is of no

small importance, especially when the eye observations are supplemented by the use of a spectroscope. This power of colouring the blowpipe flame is not, however, exhibited by all bodies with sufficient intensity to enable them to be distinguished by it with certainty, and certain substances, such as hydrochloric acid, are consequently usually employed, with barium, strontium, and calcium compounds, partly to form and partly to set free volatile compounds. By this means, however, although the intensity of the colouration is heightened, its duration is not increased, as the acid evaporates, for the most part, before it has acted sufficiently, so that the colouration lasts only for a few moments. Dr. H. Gericke overcomes this difficulty by the employment, instead of the volatile hydrochloric acid, of a chloride which will retain the chlorine at a high temperature, so that it may only be set free by degrees in small quantities, whilst the body forming its base may be without action upon the colouring power of the body under investigation. For this purpose chloride of silver appears to be the best, especially as it may readily be prepared in a state of purity. The best plan is to stir it with water into a thick paste, and keep it in a bottle.

In regard to the action of chloride of silver upon the colouration of the blowpipe flame, the author has investigated several compounds of potassium, sodium, lithium, calcium, barium, strontium, copper, molybdenum, arsenic, antimony, and lead, and mixtures of these substances. Chloride of silver has no action upon borates and phosphates.

Platinum wire does not answer well as a support, as it is soon alloyed by the metallic silver which separates, and is thus rendered useless. Silver wire is too readily fusible, and also is difficult to obtain free from copper, which may give rise to errors when in contact with the chloride of silver. Iron wire is best fitted for experiments with chloride of silver, as, from its cheapness, a new piece may be employed for each experiment, whilst the silver may be readily obtained in the form of chloride from the broken pieces.

The results obtained by the employment of chloride of silver in comparison with those obtained without this reagent are as follows:—

With potassium compounds, such as saltpetre, potashes, &c., the flame is decidedly of a darker colour with chloride of silver; and even with ferrocyanide of potassium, which, when treated by itself with the blowpipe, colours the flame blue, the addition of chloride of silver produces a distinct potassium colouration.

The action of chloride of silver upon sodium salts is not so marked, although with some, such as nitrate of sodium, common soda, and labradorite, the flame acquires a more intense yellow colour by the addition of chloride of silver. This reagent produces no observable difference with other sodium compounds, such as sulphate of sodium and analcime. This also applies to the compounds of lithium, some of which give a finer

purple-red colour on the addition of chloride of silver, whilst upon others it has no such effect.

With calcium compounds chloride of silver acts favourably upon the colouring power. Thus, the addition of chloride of silver to calcareous spar or gypsum (in the reduction-flame), gives the flame a more distinct yellowish-red colour; but stilbite gives no calcium colouration either with or without chloride of silver. With fluor-spar the colouration cannot well be observed, as this decrepitates too violently under the blowpipe.

The action of chloride of silver upon compounds of barium and strontium is decidedly advantageous, as both the intensity of the colouration and its duration leave nothing to be desired. Sicilian cœlestine, which, when heated by itself in the forceps, scarcely colours the flame, immediately produces a permanent red colouration when heated with chloride of silver.

Although it appears from the preceding statements that the employment of chloride of silver presents no advantage with some substances, it may be used with good results in the treatment of mixtures of alkalies and earths. Thus, with petalite alone, the lithium colouration is first produced, a slight sodium colouration is afterwards obtained, whilst, with chloride of silver, the sodium colouration appears very distinctly after that of lithium. With lithion-mica alone a very distinct lithium colouration is presented, but in the presence of chloride of silver, a colour is first produced, which may lead to the conclusion that potassium is present, but the lithium colouration is weakened. Ryacolite, heated by itself in the blowpipe flame, only gives a distinct sodium colouration; but with chloride of silver, a slight potassium colouration is first produced, and the colouration of sodium then appears very distinctly; the calcium contained in it cannot, however, be detected by the colouration of the flame, although evident in the spectroscope.

Chloride of silver may be employed with still greater advantage with the following metals, but in these cases it is particularly necessary that the operator should become familiar with the colour as well as the spectrum produced by each individual substance.

With copper compounds, such as red copper ore, malachite, copper pyrites, sulphate of copper, &c., when contained in other minerals, so as to be unrecognisable by the eye, the employment of chloride of silver may be of great service, as the smallest quantities of copper, when treated with chloride of silver under the blowpipe, give a continuous and beautiful blue colour to the flame. With chloride of silver, the presence of copper may be distinctly ascertained by the blowpipe, even in a solution which is no longer coloured blue by the addition of ammonia.

The employment of chloride of silver will be equally advantageous with molybdenum, as in this case also the flame gains greatly in intensity. Arsenic, lead, and antimony, are already sufficiently characterised, the

former by its odour, the two latter by their fumes; but even with these metals chloride of silver may be employed with advantage, to render their reactions still more distinct. It is only necessary to observe that the greenish-blue flame of antimony appears greener and more like that of molybdenum under the influence of chloride of silver.

Chloride of silver may also be employed with compounds containing several of the above-mentioned metals. If bouronite be heated in the oxidation-flame of the blowpipe, a fine blue flame is first produced, which indicates lead with certainty; if chloride of silver be now applied, copper is also readily shown. The antimony contained in bouronite cannot be ascertained by the colouration of the flame; but this may be easily detected upon charcoal or in a glass tube open at both ends. Native molybdate of lead without chloride of silver only gives a blue colour to the blowpipe flame; with chloride of silver this blue colouration of lead comes out more distinctly, but at the same time the tip of the flame, particularly when the reduction flame is employed, appears of a beautiful yellowish-green colour from molybdenum. With mixtures of arsenic and copper, or antimony and copper, the flame first appears a greyish-blue or greenish-blue colour, from the oxidation of the arsenic or antimony; the copper may be then very easily detected by chloride of silver. This applies also to mixtures of arsenic and molybdenum, or antimony and molybdenum; with chloride of silver the yellowish-greeen flame of molybdenum appears distinctly. It will be more difficult to analyse mixtures of arsenic and lead, or antimony and lead, in this manner, and if a compound contain both arsenic and antimony, these two bodies are not to be distinguished with chloride of silver under the blowpipe.

Chloride of silver is particularly to be recommended in testing metallic alloys for copper. Thus to test silver for copper, chloride of silver may be applied to the ends of silver wires, and on the application of heat the smallest quantity of copper will furnish a distinct reaction. This is as sensitive as any of the known copper reactions, and may be performed quickly and easily. In testing metallic alloys for traces of copper, it may be advisable to submit those which contain antimony, zinc, lead, and other volatile metals, to roasting, so as to drive off these metals before the addition of the chloride of silver.

A New Method of Quantitative Chemical Analysis.

In comparing together the results of a large number of chemical analyses it is seen that the numbers obtained vary between 99·17 to 100·67, giving a difference of about 1·5 per cent, or, supposing a quantity of 1·500 grms. of substance has been taken and the weighings carried to 0·0001 grm., a difference of 225 units. The analyses here alluded to are by no means

those which would be called bad or indifferent, but are such as have been made and published by eminent chemists. It ought further to be remembered that very many analyses yield results varying from 97 to 102 per cent, instead of 100, whilst the really bad ones never see the light at all. Under ordinary circumstances slight differences do not usually affect the result of an analysis, but if it is desired to employ the sum of the substances found to control the results, an incorrect total fails to serve this purpose, as there is no means of knowing upon which of the substances the error really falls. Moreover, in many instances, only small quantities of material are available. A more accurate and improved method of analysis would admit of the employment of smaller quantities as well as effect a great saving of time and labour.

It would appear that neither the methods and processes in use nor the impurities of reagents are greatly at fault, because it is found that, when the same substance is analysed under exactly the same conditions, the results often differ. It would, therefore, appear that accuracy depends chiefly upon the manipulations, among the most dangerous of which may be mentioned decantation, the removal of substances from a filter, the ignition of the filter paper, and the calculation of the ash; the employment of a great number of vessels may either add something to solutions or withdraw something therefrom.

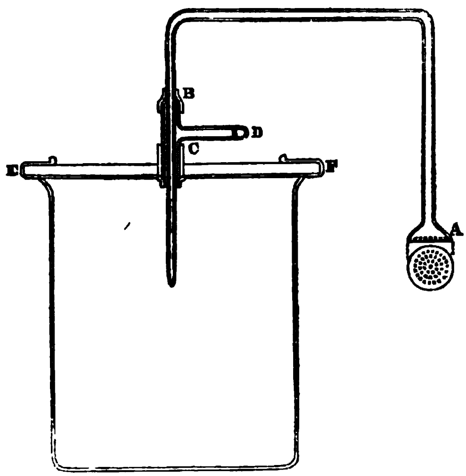
Dr. H. Carmichael has proposed a very ingenious apparatus for overcoming these difficulties. His apparatus is represented in the accompanying cuts.

Fig. 14, represented one-fourth of its natural size, consists of a doubly bent glass tube, with a funnel shaped widening at one of its ends, the wider part being perforated with a large number of small holes; the other bend of the glass tube is fitted in the T-shaped tube, B C D, closed air-tight at B, by means of a vulcanised india-rubber ring; the tube is fastened in the glass plate, E F, and fitted air-tight by means of a similar contrivance to the one just mentioned; E F is covered with a cap made of vulcanised caoutchouc, while between B and C a tube is fitted laterally, bent at D, at right angles (this part is not represented in full in the cut) and fitted with a small bored vulcanised india-rubber tube closed by a spring clamp. The cap and the ring, B, should be touched with some grease. The edges of a beaker can be readily rubbed on a piece of fine grained and thoroughly smooth and level sandstone, to take off the vitreous glaze, so that a plate of ground glass may fit quite tight thereon; this having been done the cover, E F (a ground glass plate), may be fitted so tightly that it is possible to keep in the interior of the beaker-glass as good a vacuum as in the receiver of an air-pump.

The filtering bulb, A (Fig. 15), being the most essential portion of this apparatus, its construction requires the greatest possible attention, and

should be managed as follows:—Take a glass tube having an inner bore of 2 m.m., blow at one end a thick bulb (see A, Fig. 14), flatten the bulb at the bottom, keep this bulb so hot that the glass is only slightly soft, and while in that condition make holes in it by means of a white-hot steel wire; these holes should be close together, and not larger than 0·7 m.m. The width of

FIG. 14.



the edge, *a b* (Fig. 15), differs according to the kind of filtering-paper which it is intended to use. For ordinary filtering-paper the width should be 3 m.m., for Swedish paper a width of 2 m.m. is sufficient; the perforated glass knob thus obtained is also ground slightly on sandstone. The tube to which the bulb is blown should be so bent as to make the leg B somewhat longer than the leg A; the height of the bulb must not be great, that is to say, it should be sufficiently flat to carry along with the air at the end of the filtration all the liquid into the beaker. The most suitable diameter of the bulb for general use is 2·5 c.m., the number of holes ought to be 50, but a smaller number will do when the holes are connected together by means of small channels cut in the glass by means of hydrofluoric acid. The apparatus is connected with an air-pump by means of a strong india-rubber tube. The best air-pump is formed by the human lips, but direct experiments have proved that the power of suction of men varies from 10 to 695 c.m. of mercury, that is to say, from $\frac{1}{70}$ to $\frac{9}{10}$ of an atmospheric vacuum. When the operator cannot suck above $\frac{1}{2}$ atmosphere, or when

disagreeable gases are to be worked with, the Sprengel pump or the aspirator should be used. Even when full atmospheric pressure is on, the thinnest filtering-paper will not be broken.

In order to use the apparatus the air is pumped out, water being poured simultaneously on A. The rapidity of the current thus called into play effectually removes all impurities, and the water serves also to clean the beaker. This having been done, a circularly cut piece of filtering-paper, of the same diameter as A, is pressed against A. It remains fixed there, even when the apparatus is blown into; a vacuum is again made while the filtering disc is placed in the solution of the substance to be analysed, care being taken not to let the disc touch the bottom of the vessel in which that solution is contained; as soon as the solution is filtered off from the sediment, some pure water is added, the vacuum being still maintained, after which the apparatus, with the precipitate adhering to it, is removed from the vessel in which the solution was contained, while any sediment therein remaining is transferred by careful manipulation into a previously tared crucible.

Fig. 16 exhibits the mode of the connection of the apparatus with the air-pump. The bulb is placed in the vessel, and distilled water added for

FIG. 15.

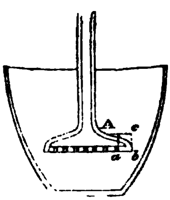


FIG. 16.

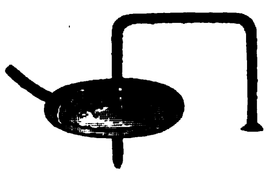
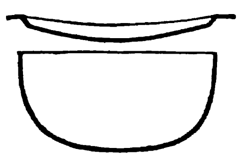


FIG. 17.

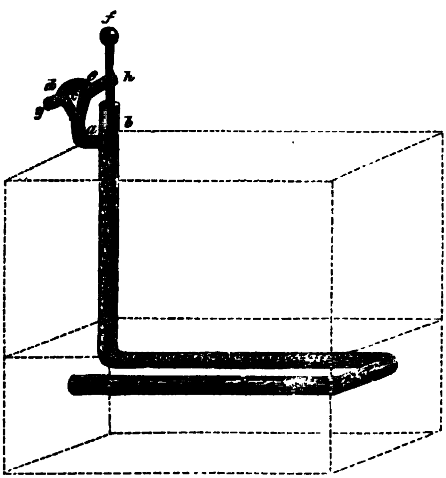


the purpose of washing the sediment thoroughly, the water running into the beaker (the vacuum being kept on) for the purpose of drying the precipitate by the current of air. This may be carried so far as to cause even gelatinous precipitates to shrink together. The spring clamp now being opened, air is admitted to the beaker, and the filtering tube removed from the crucible as well as from the cover, E F. If the operation has been properly managed, the disc of filtering-paper remains on the top of the precipitate, the upper surface of the bulb remains clean, while only a very thin and small ring of the substance adheres to the lower edge of the bulb; this substance is removed by carefully holding a piece of filtering-paper flat in the hand and pressing it gently against the bulb; turn the latter gently so as to rub all the substance on the paper, which, with the substance thus fastened to it, is thrown into the crucible. This having been done, the

crucible covered with its lid, is placed in an air-bath and heated to 105°. At this temperature the precipitate becomes readily and rapidly dry, without any danger of spirting; after which the crucible is ignited, first without the cover, until the very small quantity of paper is consumed, and afterwards with the lid on.

Although a bulb of the size above named is sufficiently large for many substances, it is preferable to have another bulb of 3·5 c.m. diameter for use with such gelatinous precipitates as alumina and peroxide of iron. Instead of the platinum crucibles in ordinary use, it is for this purpose preferable, though not indispensable, to use a platinum dish and cover, shaped as shown in Fig. 17, and weighing about 28 grms.

FIG. 18.



As the rapidity of the operations by this method makes it desirable to heat several crucibles at a time to 105°, and since this requires an air-bath with a really good gas regulator, those hitherto contrived being either of no use or somewhat expensive and too complicated, Dr. Carmichael has contrived the apparatus shown in Fig. 18. Anyone who has acquired some practice in glass-blowing may make it for his own use. Take a glass tube, 40 c.m. long and 0·6 c.m. interior diameter, bend it as shown in the woodcut so as to admit of two of the bends being placed below the false bottom of the air-bath, and the third, the vertical bend, to pass through an opening out of the bath, but so as not to touch the metal the bath is made of; at *a*, a glass tube of 2 m.m. interior diameter is melted on the wider tube, and

shaped as shown at *c*; this narrower tube is branched off into two parts, each so bent as to be on a level together. At *d* and *e* holes are made in these branches in such a manner as to form small nipples towards the outside, which are next nearly closed, and then connected together by means of an india-rubber tube; the lower end of the wide glass tube is sealed, and the top opening closed with a cork, into which, through a carefully made hole, a thin and long glass rod is fitted; the cork should extend to *a b*, so as to exclude air. This contrivance is entirely filled with mercury, and next freed from any adhering air and moisture by heating over a spirit flame; one of the open tubes at *h* and *g* is in connection with a gas supply-pipe fitted with a tap, the other open glass tube with a burner, while the openings at *d* and *e* are so small that the gas which may pass through them is too small in quantity to heat the bath to any extent, whilst, at the same time, these openings serve to prevent the sudden extinguishing of the flame by the rapid expansion of the mercury.

The apparatus is used in the following manner:—The bath is heated by a gas-burner, until the thermometer connected with the bath indicates nearly the requisite temperature; this having been reached, the glass rod, *f*, is pressed down into the mercury contained in the wider tube, until the mercury at *a* nearly touches the part *c*, which should be made as straight (not rounded) as possible. The sensitiveness of this contrivance depends, of course, upon the quantity of the mercury and its adjustment of surface; but if the apparatus is made with care, according to the directions just described, the bath remains to a fraction of a degree at a constant temperature, even in a draught of air or with a change of pressure of gas. The cooling of the mercury in the narrow tubes prevents oxidation of the metal anywhere in the tube.

The following advantages are obtained by the use of the filtering bulb:—

1. The decantation of liquids is avoided.

2. The washing, ignition, and calculation of the filter-ash is entirely dispensed with. For, since the quantity of ash contained in a filter made of the best paper, and of 12 c.m. diameter, amounts to 0·0005 grm., the ash contained in a disc of filtering-paper, as used with this apparatus, would only weigh 0·00002 grm., and even if the paper were of a commoner quality it would make no difference.

3. The velocity of filtration is very great; the water flowing into the beaker in so uninterrupted a current that it appears as if no paper disc were present. When precipitates are to be filtered off, the velocity is somewhat less; but it is then far more rapid than by the ordinary plan, and not less rapid than by Bunsen's method.

4. Since the filtering-tube dips under the fluid, no air can pass though the precipitate until it has been completely washed.

5. When a mineral has been dissolved, or when two substances have to be separated from each other, instead of, as is done by the ordinary method, placing them in a beaker to be further treated, the precipitate by this method remains in the crucible, and can be ignited directly after filtration.

6. This apparatus serves as a filtering-stand, and also as a syphon and pipette.

7. The whole apparatus may be readily kept from dust, and, if required, any gas can be readily admitted to protect a fluid to be filtered from contact with air, while a boiling solution can also be readily filtered.

8. Even so small a quantity of substance as a couple of milligrammes is sufficient for analysis. With so small quantities the entire precipitate remains fixed to the filtering disc, and may be burnt on the lid of a crucible, while any other very small portion of the substance which may adhere to any part of the apparatus may be readily removed and estimated.

9. The use of this apparatus, and the employment of small quantities of substance for analysis, occupy only about one-third of the time as compared with that required for analyses done by the ordinary plan. As an instance of the advantage of employing this method of analysis, the author quotes the following:—A mixture was taken of magnesia, chloride of potassium, and common salt, adding thereto some hydrochloric acid so as to convert the magnesia into chloride, expelling any excess of that acid by a gentle heat. The dry saline mass was re-dissolved in water, and oxide of mercury added. The mass was next gently heated in a covered crucible, until all the mercury was volatilised, and the dry residue again treated with water and filtered by means of the filtering-tube above described, by which operation the magnesia was left behind in the crucible. It was then dried in the air-bath and ignited. The solution of the alkalies was next treated in the usual manner with chloride of platinum and alcohol, and the platino-chloride of potassium, after having been separated from the fluid by the filtering-tube, dried at 105°. The small filtering-paper disc, to which hardly a particle of the salt adhered, was removed, and the platino-chloride of potassium, first ignited by itself alone, and afterwards with the addition of the paper disc; the result being that the organic matter of the paper was sufficiently large to cause the reduction of the platinum to the metallic state. The materials left in the crucible were washed with hydrochloric acid to remove any trace of magnesia, and again ignited; the platinum in the filtrate was also reduced to metal, and the chloride of sodium present determined in the usual way, care being taken to remove and estimate the very small quantity of magnesia by means of phosphate of sodium, and to deduct the weight of the magnesia thus estimated from the weight of the chloride of sodium.

The results were as follows:—

	Quantities taken.		Quantities found.
MgO	0·0690 grm.	..	0·0688 grm.
KCl	0·1873 "	..	0·1852 "
NaCl	0·0876 "	..	0·0900 "
	0·3439		0·3440

It appears that the chloride of magnesium was completely converted into magnesia again, notwithstanding the small loss of this substance due to the solubility of some of it in the alkalies present; that the quantity of the potassium salt found was deficient is accounted for by the fact that the salt was only washed with dilute alcohol, without any addition of ether to lessen the solubility of the platino-chloride of potassium. The author analysed twice a portion of a mineral, skolezite, from Scotland, taking in the first case 0·985 grm. of substance, and in the other 0·0807 grm., the result being that the percentage composition of the substance was found to be:—

	I.		II.
Silica	46·20	..	46·35
Alumina	26·28	..	26·21
Lime	9·22	..	9·17
Soda..	5·16	..	5·10
Water	13·25	..	13·45
	100·11	..	100·28

In reference to the difference of the quantity of water, the author observes that the substance had been kept for several months under a desiccator. It is clear that the principle of the apparatus above described may be applied to qualitative analysis, and also in technology on a larger scale, for which purpose a porcelain plate perforated with small holes may be used with a disc of filtering-paper.

Elementary Organic Analysis.

Founded on the Analysis of the Gaseous Products.—Dr. P. Schultz burns the substance to be analysed with chlorate of potassium in a tube, having previously sealed and exhausted it; then submits to analysis the gaseous mixture produced. The advantage of this method is the small amount of material necessary; the analyses cited as examples having been performed with from 5 to 13 milligrammes of matter.

Introduce the mixture, together with a weighed quantity of chlorate of potassium, rather more than enough for complete combustion, into a combustion-tube, sealing it at one end, and drawing it out at the other; after having exhausted and measured the pressure of the remaining air, seal the

tube, shut it up in a gun-barrel, and heat it to a dull red heat for twenty minutes. When cold, break the point of the tube under mercury, and collect the gas in a eudiometer. By measuring the quantity of gas formed, and absorbing the carbonic acid by potash, all the elements are found necessary for the calculation of the composition of an organic body containing only carbon, hydrogen, and oxygen. If the carbon absorbs its proper amount of oxygen, and the compound is a body corresponding to a hydrate of carbon, such as starch, the gaseous material obtained is exactly equal to the amount of oxygen supplied by the chlorate of potassium used. If more gas be found, it is because the body contains more oxygen than is needed to burn all its hydrogen; if, on the contrary, there is less gas, it is because the body contained an excess of hydrogen with respect to its oxygen in the constitution of water. In the combustion of nitrogenous matters, nitrogen may be obtained (after an estimation of the carbonic acid) by absorbing the oxygen with a stick of phosphorus, but the results are not very correct.

By Combustion in a Stream of Oxygen Gas.—Mr. C. M. Warren has devised the following method for performing combustions in a stream of oxygen gas.

Were it not for the danger of explosions in the combustion-tube, the occurrence of which would, at least, render its use fruitless of good results, the employment of pure oxygen, as a combustion agent in analysis, would seem, of all substances, the one most naturally suggested. This apparent difficulty is probably the chief reason it has not long ago been brought into general use; its employment since the time of Prout having been mostly confined to the combustion of the residual carbon of highly carbonaceous substances, after the other decomposition products, containing the hydrogen, had been burnt at the expense of oxide of copper.

By a very simple device Mr. Warren entirely obviates the danger of explosion—viz., the combustion-tube is closely packed with asbestos, or other inert substance, and yet so loosely as to leave free passage for gases through the interstices. The packing of the tube requires some care. This, however, may be readily accomplished, giving great uniformity to the mass of asbestos, by having the latter carefully broken into small loose pieces, which are gradually added to the tube, and arranged in position by means of a stiff iron wire. Little attention need be had to the packing of the centre of the tube, as this will come right of itself, if the packing against the sides is properly done. It will be found convenient and expeditious to turn the tube continuously in the hand, and cause the end of the iron rod to follow around against the sides of the tube, placing the asbestos, by gentle taps, alongside its inner surface, so that only very small open spaces may be seen. Generally about ten or twelve inches in length of the tube are filled with asbestos. As the combustion takes

place within a very short space, it would seem at first that the tube might be reduced considerably below the ordinary length; it is found, however, that shortening of the tube below a certain limit makes it difficult to control the distillation of volatile substances and prevent too rapid combustion; it being essential in this, as in other processes, that the combustion should proceed slowly, and with a good degree of regularity, otherwise it would be difficult to regulate the supply of oxygen to meet the demand of the burning substance. By having the column of asbestos of considerable length, the anterior end of which only is ignited, the substance, if volatile, becomes diffused through a large space, and the distillation thereby easily controlled; as only a small portion of the substance need then be heated at a time. Doubtless a shorter tube would answer equally well for many non-volatile substances. It will be observed that the asbestos packing is but another application of the principle involved in the use of wire gauze in Davy's safety-lamp.

In order to obtain perfect control of the analysis, and to be always certain that the requisite quantity of oxygen is being admitted, the following simple expedients have been adopted.

1. The distillation of the substance, if volatile, is effected by means of a bar of copper placed over and attached to one of Bunsen's burners, as shown at *a* in the accompanying figure.

This bar, having first been brought to the maximum temperature which the lamp is capable of producing, is placed near or under the bulb containing the substance; applying that part of the bar nearest or most remote from the flame, or an intermediate point, according to the temperature required.

The steadiness of the heat thus applied, and the facility with which it may be regulated by simply moving the bar, render it decidedly preferable to any other means which can be employed for that purpose. In some cases a bar of copper laid on the combustion furnace,* one end projecting

* Mr. Warren speaks strongly in favour of Baumhauer's gas furnaces, procured from Luhme and Co., in Berlin. He says it is impossible to conceive what objection one could have to it, unless it be that a naked tube might become over-heated along the bottom; and this would be a valid objection if the remedy were not so simple. If the tube be laid in a trough of sheet iron (brass is objectionable, in this process, on account of its obscuring the tube with oxide of zinc), with a thin layer of asbestos between, and fastened together with wire, no harm can ever occur from overheating. A tube of Bohemian glass, thus protected, may be used for a large number of analyses; and, indeed, become almost a permanent fixture upon the furnace. The asbestos prevents the glass and metal from adhering together —which is probably the chief or only cause of breakage of wrapped tubes—so that sudden cooling and re-heating may take place with perfect security. It is important that the iron trough should not extend much backward of that part of the tube where it is desired that the combustion should take place, so that the temperature of the principal part of the column of asbestos may remain under the control of the operator, by means of the heated copper bar or otherwise. Independent of the use of a metallic bar, as described above, or


B
c

into the flame by which the tube is being heated, and the other end raised and extending towards the substance, has been found to answer a good purpose.

2. In the case of volatile bodies, the combustion proceeds most satisfactorily when, having first heated about four or five inches of the anterior portion of the tube, which includes the oxide of copper, and started the flow of oxygen, the heated bar is applied to the bulb containing the substance. The whole of the liquid is immediately expelled, and is at once absorbed by the asbestos. Then, if necessary, gradually move the heated bar forward, driving the substance towards the ignited portion of the tube, until it shall have reached that point in the tube where the temperature is just sufficient to cause the oxygen to take up the vapour in suitable proportion; indicated by the bubbles of oxygen and carbonic acid, as described further on—a point as easily found, as to find, in the old process, the requisite temperature for proper distillation of the substance. When this is accomplished, which will occupy but a short time, the heat in front of and behind the substance being constant and uniform, no furthur manipulation of the heat is required, the supply of oxygen only requiring attention. In the ordinary way, on the contrary, in which the heat is applied only on one side of the substance, the latter, if volatile, is constantly changing position backward in the tube, necessitating a corresponding movement of the heat in the same direction, which requires constant care and considerable skill.

This procedure—referring to the immediate expulsion of liquid from the bulb, &c.—implies that that portion of the tube immediately forward of the bulb should not be already too warm, which might easily be the case with a body of very low boiling-point. It would then be necessary to expel the substance from the bulb no faster than the oxygen would absorb it in the proper proportion; which, as experience has shown, may be easily accomplished.

With a body of extreme volatility it may even be necessary to place a dish containing pieces of ice under the bulb; as even the temperature of

any novel appliance, the heat can be regulated by this furnace with as great or even greater nicety than by the use of coal. The partitions in this furnace between the cocks are two inches apart; so that the gas from one of the jets ignites about two inches of the tube. To rely, therefore, alone upon the cocks for regulating the heat in burning the substance would doubtless often lead to bad results; but the heat may be made to approach the substance in the most gradual manner—next to that of conduction by a metallic bar—by making use of a piece of thin brass plate, about two inches long, and half an inch wider than the top of the furnace, the edges of which are turned down against the sides. If this plate is laid on the wire gauze covering the furnace, and pressed down, so as to fit closely enough to prevent the gas from igniting under it, the gas escaping from the cock underneath may all be made to burn at one end of the plate, and to extend the heat along the tube as gradually as the plate itself is capable of being moved.

the surrounding air might in such a case cause the substance to pass forward too rapidly.

3. The oxygen is admitted through Liebig's potash bulbs containing sulphuric acid; and the carbonic acid formed is absorbed by similar bulbs with potash; to which is attached a tube filled with soda-lime and chloride of calcium, to take up any traces of carbonic acid which may escape absorption in the bulbs, and the trace of moisture which is invariably carried forward from the latter. Special care should be taken to select both sets of bulbs with the view to have the openings in the one as nearly as may be of the same size as those of the other, so that the bubbles of oxygen, considered as representing volumes, entering the sulphuric acid bulbs, may be readily compared with the bubbles or volumes of carbonic acid entering the potash bulbs; these bubbles may then serve as a valuable index by which to regulate the supply of oxygen. Especially is this true in cases where the composition of the body to be analysed is pretty nearly known, as then the number of bubbles of oxygen required for every bubble of carbonic acid produced may be readily calculated.

But as it is, in any case, advisable to conduct the experiment so that there shall always be an excess of oxygen passing unabsorbed through the potash bulbs, and as this excess would seldom be large even if a sufficiency of oxygen were admitted to burn the most richly hydrogenised body known, it may generally be well to admit enough for such a case.

The volume of oxygen actually consumed in burning the lightest liquid known—probably of the formula C_8H_{10}—which has been separated from petroleum, and which contains a larger percentage of hydrogen than any other non-gaseous body, as compared with the volume of carbonic acid formed, is 1·62 : 1; the fraction representing the oxygen which is taken up by the hydrogen of the body, and which of course becomes condensed and disappears from the volume of carbonic acid. In burning this body with just the equivalent quantity of oxygen—assuming that the combustion would be complete under such circumstances—we should have one bubble or volume of carbonic acid entering the potash bulbs for every 1·62 bubbles or volumes of oxygen entering the sulphuric acid bulbs. A sufficient excess of oxygen would be secured in this case, and a simple ratio obtained, if 2 bubbles of oxygen were to be admitted for 1 bubble of carbonic acid appearing in the potash bulbs. The case would then be further simplified by having the openings in the sulphuric acid bulbs of such size as would give bubbles twice as large as those from the potash bulbs; as then, when the bubbling should be equally rapid in both, the relation between the volumes of the gases would still be maintained—viz., 2 vols. of oxygen to 1 vol. of carbonic acid.

4. As an additional control over the supply of oxygen, and serving also

as a temporary safeguard against the escape of incompletely oxidised substance, in case of too rapid distillation with an insufficient flow of oxygen, two or three inches in length of the tube are filled with coarse, strongly ignited oxide of copper, placed in front of the asbestos, and this is followed by a plug of the latter substance to keep it in place, and prevent the formation of a channel along the upper surface of the oxide of copper. The tube itself being laid in an iron trough, as already described, with the upper half of the tube exposed, the oxide of copper is heated in such a manner that any reduction would be readily observed at the end in contact with the asbestos. In this manner it serves as a valuable indicator by which to determine at a glance whether the flow of oxygen is sufficient. It will rarely happen that any reduction of the oxide of copper will take place.

In some earlier experiments, with too short a column of asbestos, and ill-adapted bulbs, so much of the oxide of copper has been reduced that combustible gases have passed through the absorbing apparatus; and in one instance, when the unabsorbed gases were collected, the quantity of combustible gas was so considerable as to form with the oxygen collected with it—which of course came forward at an earlier or later stage of the process—an explosive mixture. Having seen no indications that any other than gaseous bodies escaped the combustion-tube in such a case, it occurred to Mr. Warren that such an analysis might be saved by collecting the gas over mercury, and, at the close of the combustion, before detaching the absorbing apparatus, conducting it a second time through the combustion-tube.* As a matter of economy, also, in the saving of the excess of oxygen, when a considerable number of analyses are to be made, this idea seemed to recommend itself; as the oxygen would, at the same time, become purified from any traces of combustible matter which might be present, and could then safely be collected as pure oxygen, and finally transferred to the oxygen gasometer.

For this purpose the apparatus was therefore constructed as represented in the background of the figure (see p. 438) as attached to the anterior end of the absorption apparatus. At the close of the combustion, when only pure oxygen appears to enter the potash bulbs, the flow of oxygen is interrupted; the communication with that portion of the drying apparatus which is back of the short U-tube, A, is closed at *b*; and the tube B—which is movable in the cork—turned up.† The joint at *c* is then disconnected;

* As the time consumed in an experiment is so short, and the quantity of combustible gas present, if any, so very small, and that mixed with a very large quantity of oxygen, it is not improbable that the gas might as well be collected over water; as the quantity which could be absorbed by the water in so short a space of time would probably be inappreciable.

† That this tube may not operate as a syphon, the outer limb is formed by attaching near the bend a flexible tube, of larger bore than that of the glass tube. This flexible tube

the end leading to the receiver, C, tightly closed with a piece of glass rod, and a communication established between the absorption apparatus and another receiver containing water—not shown in the figure—for collecting the pure oxygen. On opening the spring-clip, *d* (the more modern form, which is provided with a fine screw, is excellently well adapted for this purpose), the mercury will flow from the reservoir, D, into the receiver, C, and force the gas through the capillary tube, *e e*; thence through the short U-tube, A, containing chloride of calcium, to the combustion-tube and absorption apparatus; and the gas is finally collected over water in the receiver provided for that purpose.

The introduction of a longer column of oxide of copper would probably accomplish the same purpose with less expense; but neither expedient can be regarded as essential to the process. As the saving of an analysis by the use of a longer column of oxide of copper would only be occasional, the additional heat required, and consequent discomfort occasioned by its continual use, would hardly be compensated for. So that while the use of an additional quantity of oxide of copper is not to be recommended, the other expedient of collecting the gas over mercury, or water, &c., should also be discarded, unless the saving of the surplus oxygen, together with the additional security afforded, should be considered of sufficient importance to recommend it. As the passing through of the gas the second time requires no attention after it is once started, and occupies but a short time, during which the operator may attend to anything else, it may perhaps be preferable to retain in use that part of the process.

5. Some other less important peculiarities in the construction and use of the apparatus will now be noticed in connection with some remarks on the performance of the analysis.

The posterior end of the combustion-tube, as seen in the figure, is bent obliquely upward, as in the common form, except that instead of being drawn out to a point it is left of the full size of the tube. The object of this form is to prevent, in a great measure, the escape of oxygen during the time occupied in introducing the substance for analysis; and also for greater convenience and security from loss in the performance of this operation, especially in the case of volatile liquids. In the latter case the neck of the bulb—which has previously been provided with one or more scratches on its side near the end—is introduced into the end of the combustion-tube, and broken off by pressure against the side of the tube; the bulb itself is then allowed to drop in, and the end of the tube immediately closed with a

is preferable to glass on account of the readiness with which it adapts itself to any change of position of the glass tube, by which it may always project into the receiver underneath, and prevent waste of mercury.

perforated cork containing a glass tube, *f*, connecting it with the drying apparatus. This connecting tube is constructed of hard Bohemian glass, the anterior end of which is drawn out to a short, blunt point, and the opening nearly closed in the blowpipe flame, to the size of a small needle; the object of which is to increase the rapidity of the flow of oxygen at that point, and thereby diminish the liability to loss from diffusion of gases or vapour backward into the drying apparatus, which is always too liable to occur when the posterior end of the combustion-tube is not sealed.

As an additional precaution against loss from this source, this connecting tube is packed with asbestos in the same manner as the combustion-tube, and during the combustion is heated with one of Bunsen's burners. In case vapour of the substance should reach this tube, notwithstanding the above precaution against it, it could not reach the drying apparatus as such; but would be immediately decomposed, and the carbonic acid formed would at least stand a good chance of being carried forward, and prevent a loss in the determination of the carbon. The heating of this connecting tube may be superfluous for the object above described, but it certainly has the good effect of heating the oxygen, and thus preventing the condensation of liquid at the cork in the end of the combustion-tube.

In the performance of an analysis, the first step should be to expel the moisture from the combustion-tube while hot by passing through it, for some time, a stream of dry air from the gasometer.* The tube should then be filled with oxygen, before the substance, if volatile, is added; as otherwise particles of unburnt substance might escape during the displacement of the air, and occasion loss. The absorbing apparatus, having been previously weighed, is then attached, and, if the excess of oxygen employed is to be saved, the oxygen again admitted to expel the air from the absorbing apparatus. The connection is then made with the receiver, C, if used, and the tightness of the joints tested by turning down the tube B, so as to partially exhaust the apparatus. If found tight, as indicated by the liquid in the potash bulbs, the tube B is again turned up, and the substance then introduced in the manner above described. A very slow stream of

* The necessity for this may be entirely obviated, after the first analysis, and much time saved and uncertainty avoided, by connecting the anterior end of the combustion-tube, at the close of a day's operations, with a set of stationary drying tubes of ample capacity, which may stand at back of the furnace out of the way, communication with which is established by means of a flexible tube; or, better, a movable tube may be attached by means of a screw to the opening in the top of the gasometer, extending to the top of the upper reservoir, so that water cannot enter, and then, by simply turning the cock underneath, communication would be opened between the surrounding air and the combustion-tube, through the intervening drying apparatus. At the close of the work the anterior end of the combustion-tube should then be tightly corked, the fire extinguished, and the tube allowed to cool in dry air. It would thus be always ready for immediate use.

oxygen is now admitted; the tube B again turned down till the level of mercury in this tube shall be half an inch to an inch below the level of mercury in the receiver, C; and from time to time during the combustion the position of this tube is adjusted so as to preserve about this difference between the levels of the mercury, or at least so as to prevent the mercury in the tube from ever rising above that in the receiver.

In this manner the mercury, instead of offering resistance to the passage of gas from the combustion apparatus, and thus increasing the internal pressure upon the joints, which would be objectionable, actually operates advantageously by producing partial exhaustion, and thus diminishing the internal pressure upon the joints, and consequently the liability to leakage. The distillation of the substance is now commenced, and conducted as previously detailed above. So soon as condensation of moisture appears in the neck of the chloride of calcium tube, indicating that combustion has commenced, the flow of oxygen may be gradually accelerated to keep pace with the progress of the combustion, as indicated by the bubbles in the potash bulbs. When the burning of the substance seems to have been completed, heat is gradually applied, for a short time, along the whole length of the column of asbestos, to obviate the possibility of any loss from unburnt substance.

The absorbing apparatus may be weighed filled with either oxygen or air; the latter is perhaps to be preferred, as, on the whole, more convenient and less liable to lead to error. At the close of the analysis, therefore, expel the oxygen from the apparatus by admitting air from the air-gasometer,* saving for further use the oxygen which is expelled during the first five or six minutes.

Mr. Warren has chiefly employed this process in the analysis of volatile hydrocarbons of the formula C_nH_{n-6}; C_nH_{n+2}, &c. As a mixture of the vapours of these bodies with oxygen is highly explosive, a more severe test of the safety of the process could not be applied. In every experiment the combustion has proceeded as quietly as if burning in the open air. The results obtained are extremely accurate and uniform. Although these

* The oxygen-gasometer and the air-gasometer each having a separate drying apparatus, the time consumed in changing from one to the other is very much shortened, as the necessity for displacement of the oxygen or air—as the case may be—which is contained in the drying apparatus is avoided. Each drying apparatus consists—1st, of Liebig's bulbs, containing sulphuric acid; 2nd, of a U-tube, 15 inches high (nearly 3 feet of tube), filled with soda-lime for carbonic acid; and 3rd, of two such U-tubes (5 to 6 feet of tube), filled with chloride of calcium. The object in using drying tubes of such large dimensions is to avoid the necessity of too frequent renewal. The gasometers stand in a pan of copper, which is provided with an outlet to the sink, so that they may be filled without disconnecting from the drying apparatus; thus giving a degree of permanence to the apparatus, and saving some labour.

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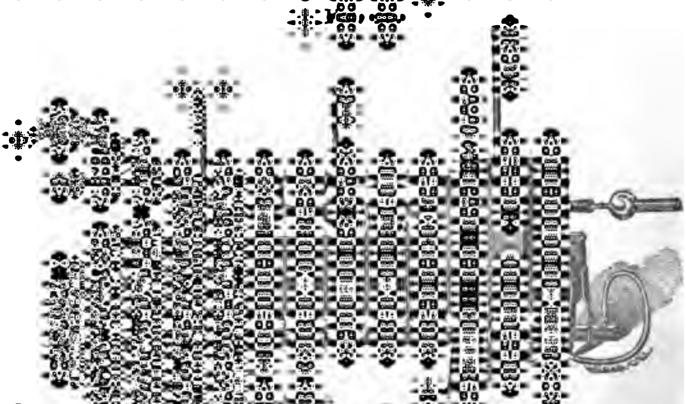

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To facilitate the removal of what may adhere to the sides of the tube, the apparatus shown in Fig. 22 will be found serviceable.

The quantity of oxide of copper or oxide of zinc required to absorb the chlorine by this process is extremely small, in consequence of its being uniformly diffused through a large mass of asbestos; hence it is obvious that but little of a solvent is needed to extract the chloride. In this respect the new process bears a striking contrast to the old one, which involves the use of a large quantity of lime, necessitating a corresponding quantity of acid, and introducing disagreeable manipulations, which tend to increase the liability to error. In the nitric acid solution the chlorine is determined in the usual manner.

The advantage which this process affords, of being able to determine the three elements carbon, hydrogen, and chlorine at a single combustion, without the introduction of any difficult or hazardous manipulation, induces the belief that it will be found preferable to any other that has been devised.

CHAPTER XV.

USEFUL TABLES.

Conversion of Centigrade and Fahrenheit Degrees.

$1° C. = 1·8° F. = \frac{9}{5}° F.$ $1° C. \times \frac{9}{5} = 1 F.$ $1° F. \times \frac{5}{9} = 1° C.$

To convert Fahrenheit into Centigrade—Subtract 32 from the original number, and divide the remainder by 1·8, thus:—$176° F. - 32 \div 1·8 = 80°$ Cent.

To convert Centigrade into Fahrenheit, multiply by 1·8, add 32 to the product, thus:—$80°$ Cent. $\times 1·8 + 32 = 176°$ F.

With the aid of a scale like the accompanying one,* thermometric degrees may be converted from one to the other with the greatest accuracy without making any calculations.

A simple inspection of the diagram will suffice to show the principle upon which the scale is constructed. Each degree Fahrenheit is divided into 5 parts, and each degree Centigrade into 9 parts, which are intended to represent fractions of a degree; the degrees themselves being numbered consecutively from the freezing point of each thermometer upwards.

A few examples will best explain the use of this scale. Suppose the temperature of a body to be 40° F. and it is required to know what degree that is on the Centigrade scale. By looking for the next degree Centigrade above 40° F. on the scale, it is found to be 4, and 4 of the small divisions after it; 40° F. are therefore equivalent to 4·4° C., or, repeating the decimal figure for greater accuracy, 4·44° C.

When Centigrade degrees have to be reduced to degrees of Fahrenheit, the decimal figures of the latter must be doubled to obtain the correct answer. For example, it is required to represent 3° C. by their Fahrenheit equivalent; referring to the scale we find the next degree Fahrenheit above 3° C. to be 37·2°, and doubling the decimal figure we have the correct answer 37·4° F. Again, taking the outer columns of figures at the same place we find 43° C. corresponding to 109·4° F.

* By Mr. Birney.

Fahrenheit.				Centigrade or Celsius.			
140	104	68	32	0	20	40	60
141	105	69	33				
142	106	70	34	1	21	41	61
143	107	71	35				
144	108	72	36	2	22	42	62
145	109	73	37	3	23	43	63
146	110	74	38				
147	111	75	39	4	24	44	64
148	112	76	40				
149	113	77	41	5	25	45	65
150	114	78	42				
151	115	79	43	6	26	46	66
152	116	80	44				
153	117	81	45	7	27	47	67
154	118	82	46	8	28	48	68
155	119	83	47				
156	120	84	48	9	29	49	69
157	121	85	49				
158	122	86	50	10	30	50	70
159	123	87	51				
160	124	88	52	11	31	51	71
161	125	89	53	12	32	52	72
162	126	90	54				
163	127	91	55	13	33	53	73
164	128	92	56				
165	129	93	57	14	34	54	74
166	130	94	58				
167	131	95	59	15	35	55	75
168	132	96	60				
169	133	97	61	16	36	56	76
170	134	98	62				
171	135	99	63	17	37	57	77
172	136	100	64	18	38	58	78
173	137	101	65				
174	138	102	66	19	39	59	79
175	139	103	67				

Tables for the Mutual Conversion of French and English Weights and Measures.

The equivalents in one system of the weights and measures of the other system can readily be found by means of the following tables. By changing the position of the decimal point, the tables are available for all decimal multiples and subdivisions of these quantities; for instance, in order to find the part of a gramme which corresponds to 0·1, 0·01, 0·001, &c., of a grain, it is necessaty to advance the decimal point one, two, three places to the left. In the same manner it is advanced to the right for the purpose of finding the grammes corresponding to 10, 100, 1000, &c., grains.

For example:—In the table for the conversion of grammes into grains, it is required to find the equivalent in grains of 6·4431 grammes.

From number 6 (without altering the place of the decimal point)	92·6304
*From number 4 (advancing the decimal point one place to the left)	6·1753
*From number 4 (advancing the decimal point two places to the left)	0·6175
*From number 3 (advancing the decimal point three places to the left)	0·0463
*From number 1 (advancing the decimal point four places to the left)	0·0015
Therefore 6·4431 grammes are equal to	99·4710 grains.

Grammes into grains.

Grammes.		Grains.	Grammes.		Grains.	Grammes.		Grains.
1	=	15·4384	4	=	61·7536	7	=	108·0688
2	=	30·8768	5	=	77·1920	8	=	123·5072
3	=	46·3152	6	=	92·6304	9	=	138·9456

Grains into grammes.

Grains.		Grammes.	Grains.		Grammes.	Grains.		Grammes.
1	=	0·06477	4	=	0·25908	7	=	0·45339
2	=	0·12954	5	=	0·32385	8	=	0·51816
3	=	0·19431	6	=	0·38862	9	=	0·58293

Pounds into kilogrammes.

Pounds.		Kilogrammes.	Pounds.		Kilogrammes.	Pounds.		Kilogrammes.
1	=	0·4534148	4	=	1·8136592	7	=	3·1739036
2	=	0·9068296	5	=	2·2670740	8	=	3·6273184
3	=	1·3602444	6	=	2·7204888	9	=	4·0807332

* In almost every case when the decimal point is moved to the left, the last figures may be omitted without introducing any appreciable error.

Inches into centimetres.

Inches.		Centimetres.	Inches.		Centimetres.	Inches.		Centimetres.
1	=	2·539954	4	=	10·1598	7	=	17·7797
2	=	5·0799	5	=	12·6998	8	=	20·3196
3	=	7·6199	6	=	15·2397	9	=	22·8596

Feet into metres.

Feet.		Metres.	Feet.		Metres.	Feet.		Metres.
1	=	0·3047945	4	=	1·2197680	7	=	2·1335614
2	=	0·6095890	5	=	1·5239724	8	=	2·4383559
3	=	0·9143835	6	=	1·8287669	9	=	2·7431504

Miles into kilometres.

Miles.		Kilometres.	Miles.		Kilometres.	Miles.		Kilometres.
1	=	1·6093	4	=	6·4373	7	=	11·2652
2	=	3·2186	5	=	8·0466	8	=	12·8745
3	=	4·8279	6	=	9·6559	9	=	14·4838

Square feet into square metres.

Sq. feet.		Sq. metres.	Sq. feet.		Sq. metres.	Sq. feet.		Sq. metres.
1	=	0·0929	4	=	0·3716	7	=	0·6503
2	=	0·1858	5	=	0·4645	8	=	0·7432
3	=	0·2787	6	=	0·5574	9	=	0·8361

Cubic feet into cubic metres.

Cub. feet.		Cub. metres.	Cub. feet.		Cub. metres.	Cub. feet.		Cub. metres.
1	=	0·028314	4	=	0·113256	7	=	0·198198
2	=	0·056628	5	=	0·141570	8	=	0·226512
3	=	0·084942	6	=	0·169884	9	=	0·254826

Long tons into tonnes of 1000 kilos.

Long tons.		Tonnes of 1000 kilos.	Long tons.		Tonnes of 1000 kilos.	Long tons.		Tonnes of 1000 kilos.
1	=	1·015649	4	=	4·062596	7	=	7·109543
2	=	2·031298	5	=	5·078245	8	=	8·125192
3	=	3·046947	6	=	6·093894	9	=	9·140841

Pounds per square inch into kilogrammes per square centimetre.

Pounds per sq. inch.		Kilos. per sq. centim.	Pounds per sq. inch.		Kilos. per sq. centim.	Pounds per sq. inch.		Kilos. per sq. centim.
1	=	0·0702774	4	=	0·2811096	7	=	0·4919418
2	=	0·1405548	5	=	0·3513870	8	=	0·5622192
3	=	0·2108322	6	=	0·4216644	9	=	0·6324966

Kilogrammes per square millimetre into pounds per square inch.

Kilos. per sq. millim.		Pounds per sq. inch.	Kilos. per sq. millim.		Pounds per sq. inch.	Kilos. per sq. millim.		Pounds per sq. inch.
1	=	1425·45	4	=	5701·80	7	=	6978·15
2	=	2850·90	5	=	7127·25	8	=	11403·60
3	=	4276·35	6	=	8552·70	9	=	12829·05

Relative Values of French and English Weights and Measures.

Weights.

Milligramme	=	0·015438395	troy grain
Centigramme	,,	0·15438395	,, ,,
Decigramme	,,	1·5438395	,, ,,
Gramme	,,	15·438395	,, ,,
,, ...	,,	0·643	pennyweight
,, ...	,,	0·03216	oz. troy
,, ...	,,	0·03527	oz. avoirdupois
Decagramme	,,	154·38395	troy grains
,, ...	,,	5·64	drams avoirdupois
Hectogramme	,,	3·2154	ozs. troy
,, ...	,,	3·527	ozs. avoirdupois
Kilogramme	,,	2·6803	lbs. troy
,, ...	,,	2·205486	lbs. avoirdupois
Myriagramme	,,	26·803	lbs. troy
,, ...	,,	22·05486	lbs. avoirdupois
Quintral metrique	,,	100 kilogs. =	220·5486 lbs. avoir.
Tonne	,,	1000 ,,	,, 2205·486 ,,

Different authors give the following values for the gramme :—

Gramme	=	15·44402	troy grains
,,	,,	15·44242	,,
,,	,,	15·4402	,,
,,	,,	15·433159	,,
,,	,,	15·43235	,,

Avoirdupois.

Long ton = 20 cwts. = 2240 lbs.	=	1015·649	kilogrammes
Short ton (2000 lbs.)	,,	906·8296	,,
Hundredweight (112 lbs.) ..	,,	50·78245	,,
Quarter (28 lbs.)	,,	12·6956144	,,
Pound = 16 ozs. = 7000 grs.	,,	453·4148	grammes
Ounce ,, 16 drams ,, 437·5 grs.	,,	28·3375	,,
Dram ,, 27·344 grains	,,	1·77108	,,
Grain	,,	0·064773	,,

Troy (Precious Metals).

Pound	=	12 ozs.	=	5760 grs.	=	373·096 grammes
Ounce	„	20 dwts.	„	480 „	„	31·0913 „
Pennyweight	..		„	24 „	„	1·55457 „
Grain	..	..	„	.. ..	„	0·064773 gramme

Troy (Pharmacy).

Ounce	=	8 drams	=	480 grs.	=	31·0913 grammes
Dram	„	3 scruples	„	60 „	„	3·8869 „
Scruple	„	.. ..	..	20 „	„	1·29546 „

MEASURES OF LENGTH.

Millimetre	=	0·03937	inch
Centimetre	„	0·393708	„
Decimetre	„	3·937079	inches
Metre	„	39·37079	„
„	„	3·2808992	feet
„	„	1·093633	yard

Inch ($\frac{1}{36}$th yard)	=	2·539954	centimetres
Foot ($\frac{1}{3}$rd yard)	„	3·0479449	decimetres
Yard	„	0·91438348	metre
Mile (1760 yards)	„	1609·3149	„

SUPERFICIAL MEASURES.

Square millimetre	=	$\frac{1}{645}$th of a square inch		
„ „	„	0·00155	„	„
„ centimetre	„	0·155086	„	„
„ decimetre	„	15·5086	„	inches
„ „	„	0·10769	„	foot
„ metre or centiare	„	1550·86	„	inches
„ „	„	10·7698	„	feet
„ „	„	1·196033	„	yards
Are	„	1076·98	„	feet
„	„	119·6033	„	yards
„	„	0·098845	„	rood
Hectare	„	11960·33	„	yards
„	„	2·471143	„	acres

Superficial Measures (*continued*).

Square inch	=	645·109201	sq. millimetres
" "	"	6·45109	" centimetres
" foot	"	9·2903	" decimetres
" yard	"	0·836097	" metre
Acre (4840 sq. yards) ..	"	0·404671	" hectare

Measures of Capacity.

Cubic millimetre	=	0·000061029	cubic inch
" centimetre	"	0·061029	" "
10 cubic centimetres	"	0·61029	" "
100 " "	"	6·10295	" inches
1000 " " or litre	"	61·0295688	" "
" " " "	"	1·760773	imperial pints
" " " "	"	0·2200967	" gallon
Decalitre	"	610·295688	cubic inches
"	"	2·2009668	imp. gallons
Hectolitre	"	3·5317	cubic feet
"	"	22·009668	imp. gallons
Cubic metre	"	1·308	cubic yard
" "	"	35·3171	" feet

Cubic inch	=	16·3855	cubic centimetres
" foot	"	28·3159	" decimetres
" yard	"	0·764520696	" metre

British Imperial Measures.

Pint (⅛ gallon) ..	=	0·567932	litre
Quart (¼ ") ..	"	1·135864	litres
Imperial gallon ..	"	4·54345797	"

Weight of Water, &c.

1 cubic inch	252·45 grs.
1 pint (=34·65 cub. ins.)	1·25 lbs.
1 cubic foot (=6·25 galls., or 1000 ozs.)	62·50 "
1 gallon (=277·274 cub. ins.)	10·00 "
1·8 cubic feet	1 cwt.
35·84 cubic feet	1 ton.
11·20 gallons	1 cwt.
224·0 "	1 ton.

A cubic inch of Mercury = 3425·25 grs.

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